Supplementary Information

Unusual cleavage of phosphaalkynes triple bond in the coordination sphere of transition metals

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Content:

1. Experimental

All experiments were performed under an atmosphere of dry nitrogen using Schlenk and drybox techniques. $CH_3C{\equiv}P$,[1] *t*BuC≡P,[2] *i*PrC≡P[3], $[Fe_2(CO)_9]$[4] and $[Co_2(CO)_8]$[5] were synthesized according to reported literature. Solvents were freshly distilled under Nitrogen from Na/benzophenone (diethyl ether, tetrahydrofurane (THF)) and Na/K alloy (*n*-pentane, *n*-hexane, toluene and C_6D_6). IR spectra were recorded on a Varian FTS-800 spectrometer. ^{31}P NMR spectra were recorded at room temperature on a Bruker Avance 400 spectrometer (^{31}P: 161,976 MHz). ^{31}P NMR chemical shifts are reported in parts per million (ppm) relative to external standards H_3PO_4 (85%).
Elemental analyses were performed by the microanalytical laboratory of the University of Regensburg. For the EI MS, a Finnigan MAT SSQ 710 A mass spectrometer was used.

1.1. Synthesis of 1a-1c:

$[\langle\{Co_3(CO)_9\}(\mu_4\text{-}P)\rangle\langle\{Co_3(\mu\text{-}CO)_3(CO)_5\}(\mu_3\text{-}CR)\rangle]$ (R = CH_3 (1a), R = *t*Bu (1b), R = *i*Pr (1c)): A solution of $[Co_2(CO)_8]$ (**1a**: 255 mg, 0.75 mmol; **1b**: 328 mg, 0.96 mmol, **1c**: 342 mg, 1 mmol) in Et_2O (**1a**: 20 mL, **1b**: 40 mL, **1c**: 10 mL) was cooled to -80°C and a cold solution of phosphaalkyne (**1a**: 5 mL of $CH_3C{\equiv}P$ in Et_2O (0.25 mmol, c = 0.05 $molL^{-1}$), **1b**: 4 mL of *t*BuC≡P in *n*-hexane (0.032 mg, 0.32 mmol, c = 0.08 $molL^{-1}$), **1c**: 4 mL of *i*PrC≡P in Et_2O (0.33 mmol, c = 83.6 $mmolL^{-1}$) was added. The reaction mixture turned to a brownish black shade while slowly warming up to room temperature overnight. After removal of all volatiles *in vacuo*, the crude mixtures were suspended in *n*-hexane (**1a**: 20 mL, **1b**: 110 mL, **1c**: 15 mL), filtered, concentrated and stored at +5°C (**1a**, **1b**) or -30°C (**1c**). Within a week, single crystals of **1a-c** suitable for single crystal X-ray diffraction analysis were formed. Yield: **1a**: 130 mg (59%). **1b**: 86 mg (29%). **1c**: 95 mg (32%).

$[\langle\{Co_3(CO)_9\}(\mu_4\text{-}P)\rangle\langle\{Co_3(\mu\text{-}CO)_3(CO)_5\}(\mu_3\text{-}CMe)\rangle]$ (1a): $^{31}P\{^1H\}$ (C_6D_6): δ = 680 (br s, $\omega_{1/2}$ = 111 Hz); IR (KBr): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2110 (sh, w), 2102 (sh, w), 2071 (sh, s), 2029 (s), 2011 (s), 1980 (s), 1877 (sh, w), 1863 (sh, w), 1845 (m), 1826 (w), 1763 (m); IR (*n*-hexane): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2075 (m), 2066 (s), 2057 (s), 2038 (sh, w), 2027 (w); EI MS (*n*-hexane): *m/z* (%) = 888 (4) [M^+], 860 (14) [M^+-CO], 832 (50) [M^+- 2CO], 804 (100) [M^+- 3CO], 776 (56) [M^+- 4CO], 748 (42) [M^+- 5CO], 720 (41) [M^+- 6CO], 692 (8) [M^+- 7CO], 663 (1) [M^+- 8CO]; Elemental analysis calc. (%) for $C_{19}H_3O_{17}PCo_6$ (887.76 $gmol^{-1}$): C 25.7, H 0.34; found: C 25.32, H 0.35.

$[\langle\{Co_3(CO)_9\}(\mu_4\text{-}P)\rangle\langle\{Co_3(\mu\text{-}CO)_3(CO)_5\}(\mu_3\text{-}CtBu)\rangle]$ (1b): $^{31}P\{^1H\}$ (C_6D_6): δ = 695 (br s, $\omega_{1/2}$ = 200 Hz); IR (KBr): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2112 (s), 2082 (sh, s), 2064 (s), 2049 (s), 2033 (s), 2021 (s), 2009 (s), 2000 (s), 1869 (s), 1854 (s); IR (*n*-hexane): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2110 (m), 2073 (s), 2067 (s), 2052 (s), 2038 (m), 2025 (m), 2016 (s), 2006 (m), 1881 (w), 1867 (w); EI MS (*n*-hexane): *m/z* (%) = 930 (4) [M^+], 902 (2) [M^+-CO], 874 (16) [M^+- 2CO], 846 (35) [M^+- 3CO], 818 (38) [M^+- 4CO], 790 (35) [M^+- 5CO], 762 (66) [M^+- 6CO], 734 (100) [M^+- 7CO], 706 (70) [M^+- 8CO], 678 (60) [M^+- 9CO], 650 (56) [M^+- 10CO], 622 (62) [M^+- 11CO], 594 (58) [M^+- 12CO], 566 (53) [M^+- 13CO], 538 (48) [M^+- 14CO], 510 (68) [M^+- 15CO], 482 (67) [M^+- 16CO], 454 (93) [M^+- 17CO]; elemental analysis calc. (%) for $C_{22}H_9O_{17}PCo_6$ (929.87 $gmol^{-1}$): C 28.42, H 0.98; found: C 28.28, H 1.26.

[⟨{Co$_3$(CO)$_9$}(μ_4-P)⟩⟨{Co$_3$(μ-CO)$_3$(CO)$_5$}(μ_3-C*i*Pr)⟩] (1c): ^{31}P{^{1}H} (C$_6$D$_6$): δ = 684 (br s, $\omega_{1/2}$ = 105 Hz); IR (*n*-hexane): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2109 (w), 2066 (s), 2055 (s), 2046 (s), 2024 (s), 1993 (w), 1867 (m), 1858 (m); EI MS (*n*-hexane) *m/z* (%) = 915 (16) [M$^+$], 887.4 (10) [M$^+$-CO], 859.5 (20) [M$^+$- 2CO], 831.5 (54) [M$^+$- 3CO], 803.6 (43) [M$^+$- 4CO], 775.5 (44) [M$^+$- 5CO], 747.6 (90) [M$^+$- 6CO], 719.4 (100) [M$^+$- 7CO], 691.6 (54) [M$^+$- 8CO], 663.6 (49) [M$^+$- 9CO], 635.6 (50) [M$^+$- 10CO], 607.6 (26) [M$^+$- 11CO], 579.7 (23) [M$^+$- 12CO], 551.7 (38) [M$^+$- 13CO], 523.7 (30) [M$^+$- 14CO], 495.7 (38) [M$^+$- 15CO], 467.7 (42) [M$^+$- 16CO], 439.7 (58) [M$^+$- 17CO], 397 (12) [M$^+$- 17CO - C$_3$H$_7$]; elemental analysis calc. (%) for C$_{21}$H$_7$O$_{17}$PCo$_6$ (915.54 gmol^{-1}): C 27.53, H 0.77; found: C 27.31, H 0.97.

1.2. Synthesis of 2a-2b:

[⟨{Fe$_3$(CO)$_9$}(μ_3-CR)(μ_4-P)⟩⟨{Fe(CO)$_4$}⟩] (R = *t*Bu (2a), R = *i*Pr (2b)): In an ultrasonic bath, Fe$_2$(CO)$_9$ (**2a**: 837 mg, 2.4 mmol; **2b:** 455 mg, 1.25 mmol) is treated with ultrasound to dissolve in 15 mL THF. The corresponding phosphaalkyne (**2a**: *t*BuC≡P, 0.1 mL, 0.8 mmol; **2b**: *i*PrC≡P, 5 mL, 0.42 mmol) is added at room temperature. The brown reaction mixture is stirred for seven days, after which the solvent is removed *in vacuo*. The residue is extracted with five 10 mL portions of *n*-pentane and filtered over celite. The dark brown filtrate is concentrated to 3 mL and stored at 5°C. Red-brown crystals of **2a** could be obtained after a few days. Yield: **2a**: 305 mg (54%). **2b** couldn't be crystallized, the solvent was removed *in vacuo* and an oily product was obtained. Yield: **2b**: 382 mg (71%).

[⟨{Fe$_3$(CO)$_9$}(μ_3-C*t*Bu)(μ_4-P)⟩⟨{Fe(CO)$_4$}⟩] (2a): ^{31}P{^{1}H} (C$_6$D$_6$): δ = 743 (s); IR (KBR): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2045 (w), 2034 (s), 1993 (s), 1976 (s), 1960 (s); IR (toluene): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2045 (w), 2012 (w), 1998 (w), 1960 (w); EI MS (*n*-hexane) *m/z* (%) = 687.7 (17) [M$^+$], 659.7 (26) [M$^+$-CO], 631.7 (3) [M$^+$- 2CO], 603.7 (21) [M$^+$- 3CO], 575.8 (24) [M$^+$- 4CO], 547.8 (32) [M$^+$- 5CO], 519.8 (58) [M$^+$- 6CO], 491.8 (80) [M$^+$- 7CO], 463.8 (54) [M$^+$- 8CO], 435.9 (28) [M$^+$- 9CO], 407.9 (62) [M$^+$- 10CO], 379.9 (26) [M$^+$- 11CO], 351.9 (40) [M$^+$- 12CO], 323.9 (36) [M$^+$- 13CO]; HR-MS (*n*-hexane) *m/z* (%) = 687.7176 [M$^+$].

[⟨{Fe$_3$(CO)$_9$}(μ_3-C*i*Pr)(μ_4-P)⟩⟨{Fe(CO)$_4$}⟩] (2b): ^{31}P{^{1}H} (C$_6$D$_6$): δ = 735 (s); IR (*n*-hexane): $\tilde{\upsilon}_{CO}$ [cm^{-1}] = 2045 (w), 2014 (w), 2002 (w), 1951 (w); EI MS (*n*-hexane) *m/z* (%) = 673.7 (17) [M$^+$], 645.7 (24) [M$^+$-CO], 617.8 (9) [M$^+$- 2CO], 589.8 (19) [M$^+$- 3CO], 561.7 (22) [M$^+$- 4CO], 533.8 (20) [M$^+$- 5CO], 505.8 (72) [M$^+$- 6CO], 477.8 (100) [M$^+$- 7CO], 449.8 (40) [M$^+$- 8CO], 421.9 (38) [M$^+$- 9CO], 393.9 (62) [M$^+$- 10CO], 365.9 (45) [M$^+$- 11CO], 337.9 (44) [M$^+$- 12CO], 309.9 (45) [M$^+$- 13CO], 254.1 (10) [M$^+$- 13CO - Fe], 189.9 (23) [M$^+$- 13CO – Fe – C$_4$H$_7$].

1. Crystallographic data

Crystals suitable for single crystal X-ray diffraction analyses were obtained for **1a-c** and **2a** as described above. Single crystal data were acquired using either an Agilent Technologies (formerly Oxford Diffraction) Gemini R Ultra diffractometer (**1a**, **1b**) using Cu-K_α (λ = 1.54178 Å, **1b**) or Mo-K_α (λ = 0.71073 Å, **1a**) radiation from sealed tubes and a Ruby CCD detector, or at an Agilent Technologies (formerly Oxford Diffraction) SuperNova device employing a microfocus copper source with an Atlas CCD detector (**1c**, **2a**). A semi-empirical multi-scan absorption correction from equivalents[6] or an analytical[7] absorption correction from crystal faces was applied.

The data processing and integration was done with the CrysAlis software package.[6] Structure determinations were performed by direct methods with the solving programs SUPERFLIP (**1c, 2a**),[8] SIR-92[9] and SHELXS-97.[10]

All structures were refined by full-matrix least-squares based on F^2 with the program SHELXL-97.[10] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions. The refinement was carried out with isotropic displacement parameters according to the riding model. Figures were created with Olex2.[11]

Due to poor diffraction data for **1b** it could only be acquired up to a resolution of 0.9 Å. Thus, its solid-state structure can only be interpreted as structural confirmation.

CCDC-2281826 (**1a**), CCDC-2282284 (**1b**), CCDC-2281827 (**1c**), and CCDC-2281828 (**2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.1. Compound 1a

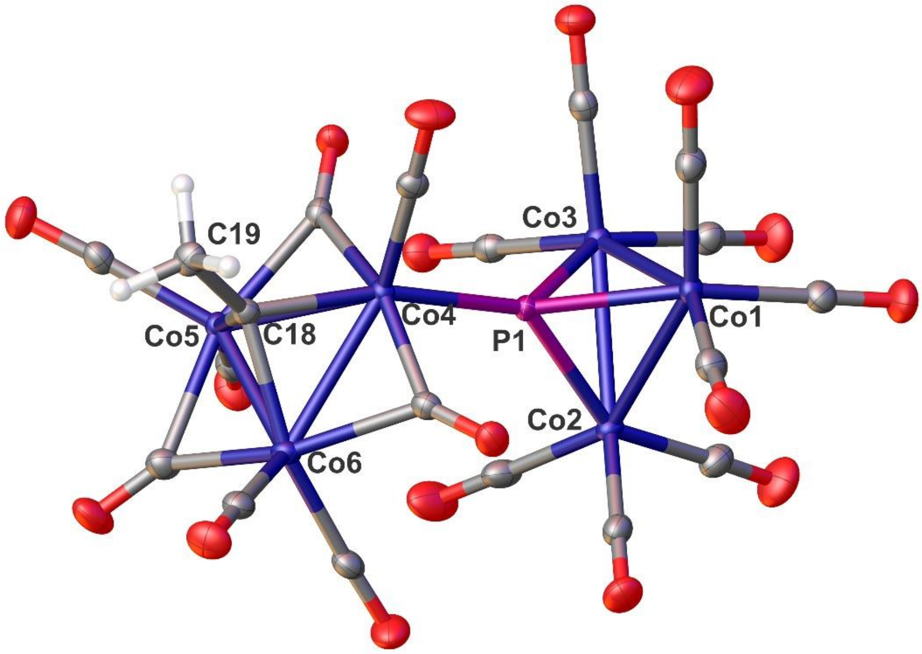

Figure S1. Molecular structure of **1a** in the solid state (50% probability level).

2.2. Compound 1b

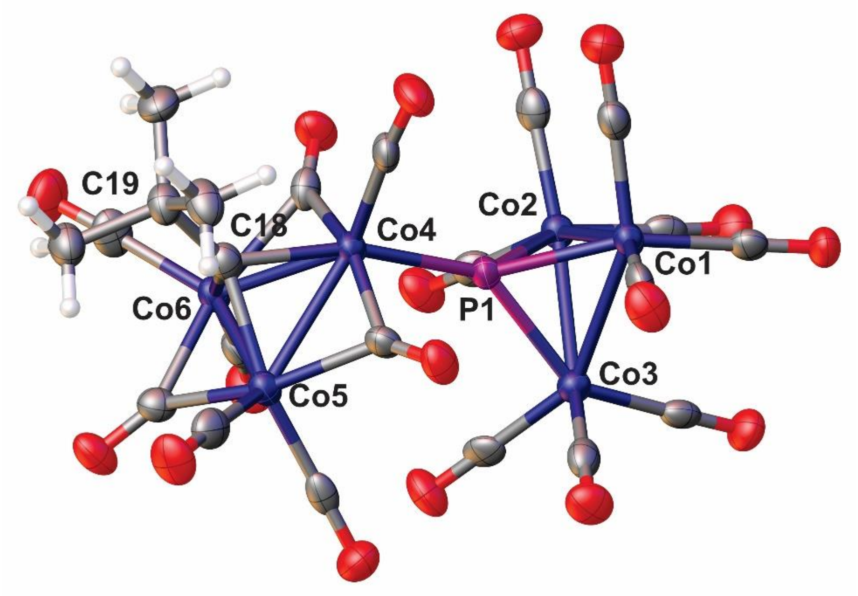

Figure S2. Molecular structure of **1b** in the solid state (50% probability level). Due to poor diffraction data for **1b** could only be acquired up to a resolution of 0.9 Å. Thus, its solid-state structure can only be interpreted as structural confirmation and bond lengths/angles must be considered carefully.

2.3. Compound 1c

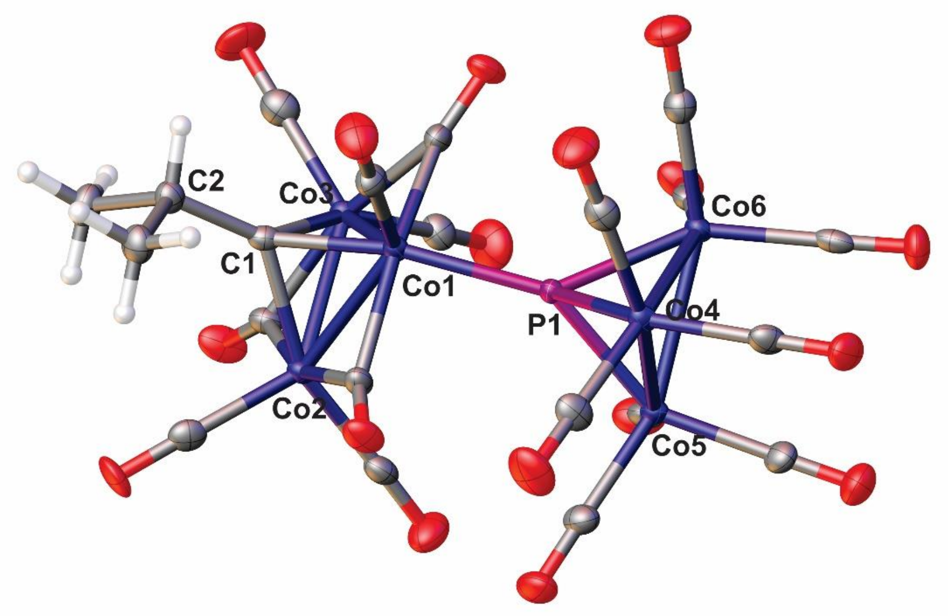

Figure S3. Molecular structure of **1c** in the solid state (50% probability level).

2.4. Compound 2a

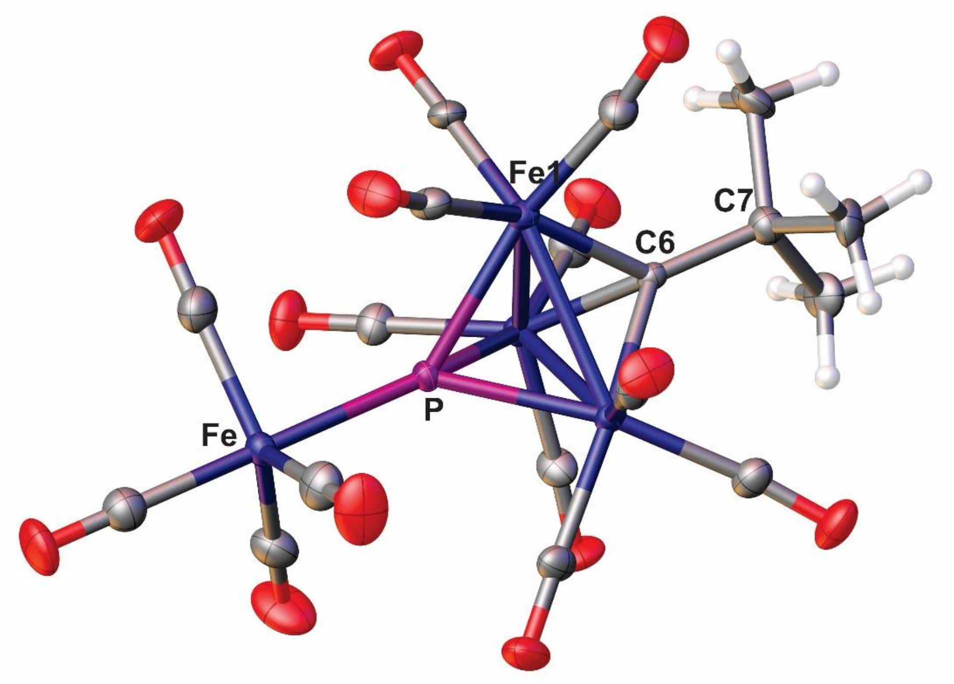

Figure S4. Molecular structure of **2a** in the solid state (50% probability level).

Table S1. Structure determination summary of complexes **1a**, **b**, **c** and **2a**.

Compound	**1a**	**1b**	**1c**	**2a**
Formula	$C_{19}H_3Co_6O_{17}P$	$C_{22}H_9Co_6O_{17}P$	$C_{21}H_7Co_6O_{17}P$	$C_{18}H_9Fe_4O_{13}P$
CCDC number	2281826	2282284	2281827	2281828
M	887.76	929.84	1513.04	687.62
T [K]	123(1)	123(1)	123(1)	123(1)
crystal system	monoclinic	triclinic	triclinic	trigonal
space group	$P2_1/c$	P-1	P-1	$R3c$
a [Å]	12.1777(2)	8.6816(6)	8.6531(4)	8.7479(4)
b [Å]	14.2641(2)	11.1058(6)	11.1862(5)	8.7479(4)
c [Å]	16.3093(2)	17.5276(11)	17.1189(8)	54.779(3)
α [°]	90	81.547(5)	88.761(4)	90
β [°]	108.715(2)	83.899(5)	79.668(4)	90
γ [°]	90	68.045(6)	68.320(4)	120
V[Å^3]	2683.20(7)	1547.93(18)	1513.04(12)	3630.4(4)
Z	4	2	2	6
colour and shape	brown-black prisms	red rods	clear red plates	dark red pyramids
crystal size [mm]	0.25 x 0.16 x 0.15	0.13 x 0.09 x 0.03	0.17 x 0.10 x 0.01	0.15 × 0.14 × 0.11
ρ_{calcd} [Mg m^{-3}]	2.198	1.995	2.010	1.887
F(000)	1720	908	892	2040
μ [mm^{-1}]	3.763	25.768	26.350	20.073
λ [Å]	0.71073	1.54184	1.54184	Radiation
diffractometer	Oxford Diffraction Gemini R Ultra	Oxford Diffraction Gemini R Ultra	Oxford Diffraction SuperNova	Oxford Diffraction SuperNova
Index ranges hkl	$-18 \leq h \leq 18$ $-22 \leq k \leq 22$ $-24 \leq l \leq 26$	$-7 \leq h \leq 9$ $-12 \leq k \leq 12$ $-19 \leq l \leq 18$	$-10 \leq h \leq 7$ $-13 \leq k \leq 13$ $-21 \leq l \leq 18$	$-11 \leq h \leq 10$ $-10 \leq k \leq 10$ $-69 \leq l \leq 67$
ϑ limit [°]	$2.32 \leq \theta \leq 34.98$	$4.32 \leq \theta \leq 58.56$	$4.258 \leq \theta \leq 72.701$	$4.84 \leq \theta \leq 76.52$
Reflections collected	22840	7513	9638	6850
Independent reflections	10854	4280	5743	1575
Data/ restraints/ parameters	10854/0/389	4280/0/418	5743/0/408	1623/1/111
Goodness-of-fit on F^2	0.906	0.893	0.933	1.032
Flack parameter x				-0.014(7)
$R(int)$	0.0226	0.0367	0.0574	0.0389
Final R indices [I>2 σ (I)]	R_1 = 0.0251 wR_2 = 0.0531	R_1 = 0.0510 wR_2 = 0.1298	R_1 = 0.0432 wR_2 = 0.1049	R_1 = 0.0413 wR_2 = 0.1078
R indices (all data)	R_1 = 0.0405 wR_2 = 0.0514	R_1 = 0.0686 wR_2 = 0.1240	R_1 = 0.0536 wR_2 = 0.1074	R_1 = 0.0421 wR_2 = 0.1086
Largest difference hole and peak [e Å^{-3}]	0.783/ -0.477	0.992/-0.636	0.760/-0.776	1.48/-0.59

1. Infrared, Mass and NMR Spectra

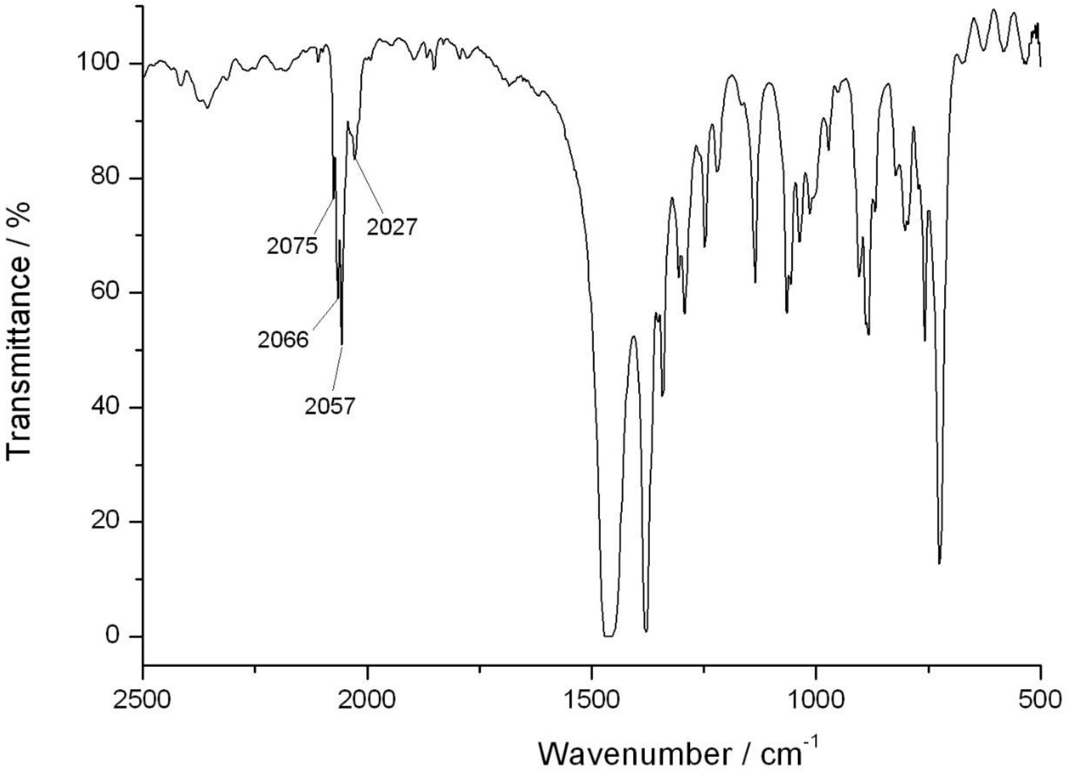

Figure S5. Section of the IR spectra of **1a** in *n*-hexane.

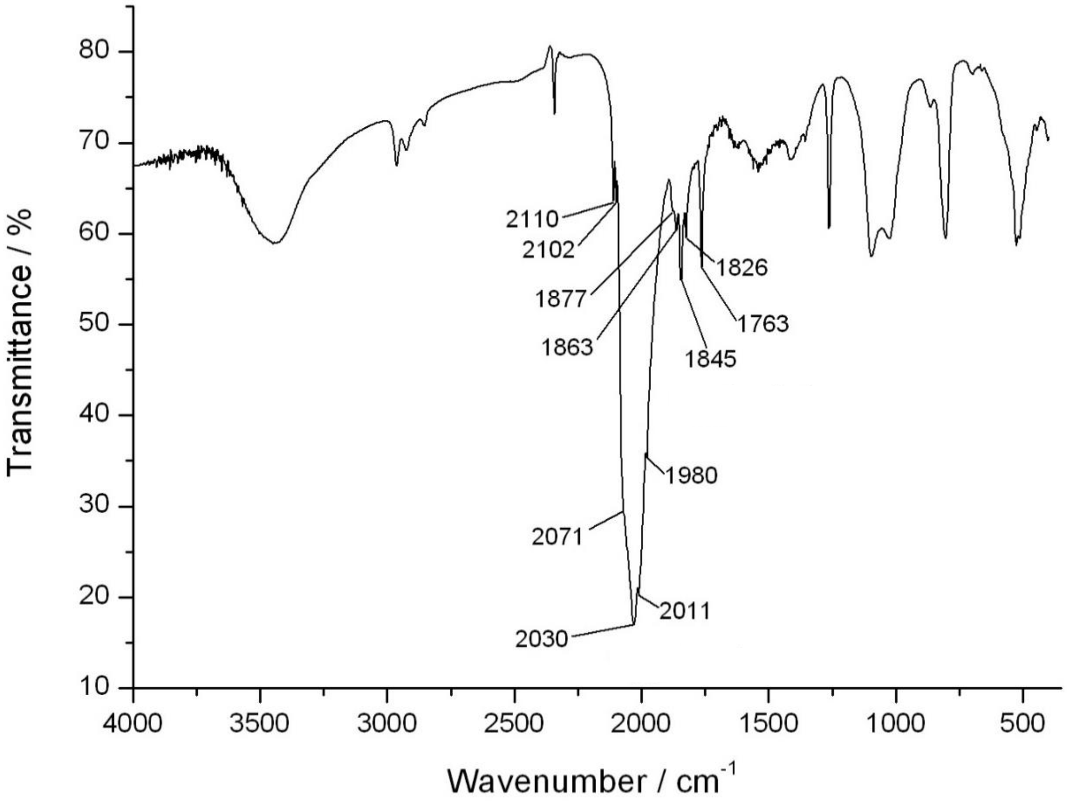

Figure S6. Section of the IR spectra of **1a** in KBr.

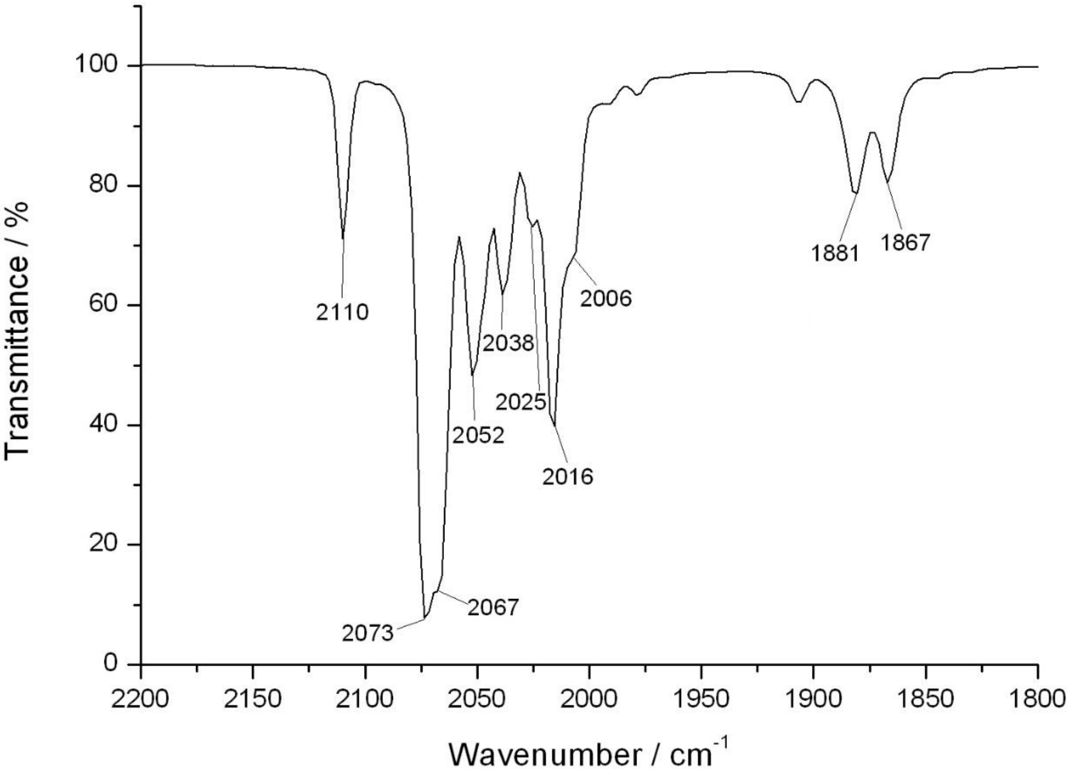

Figure S7. Section of the IR spectra of **1b** in *n*-hexane.

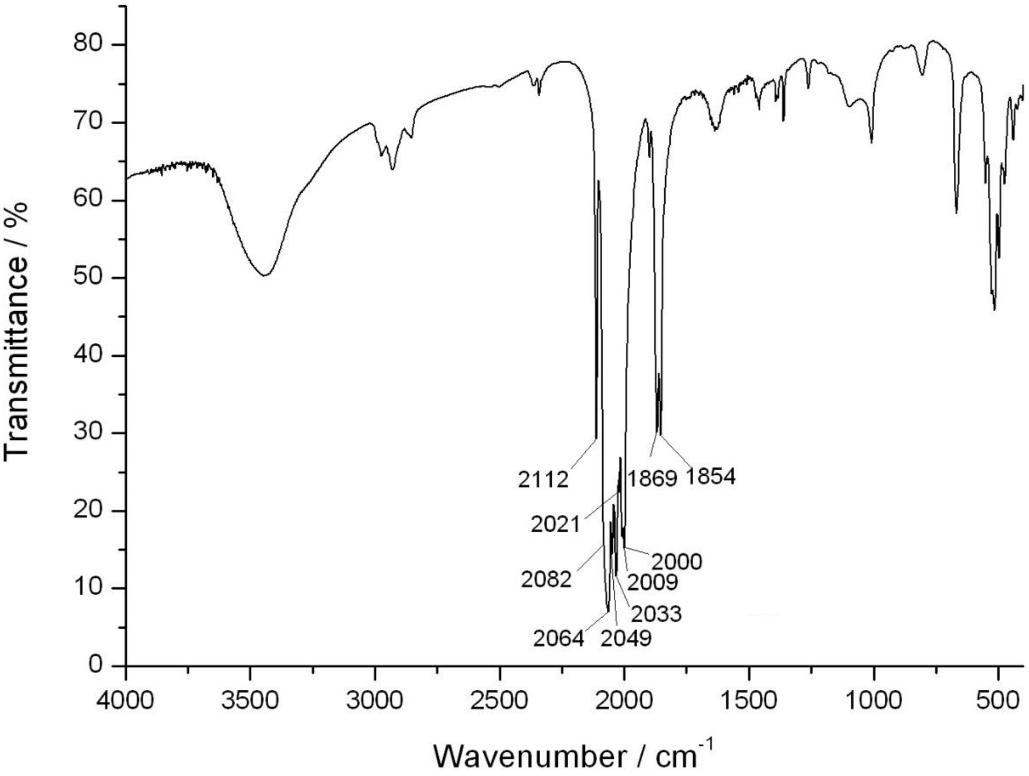

Figure S8. Section of the IR spectra of **1b** in KBr.

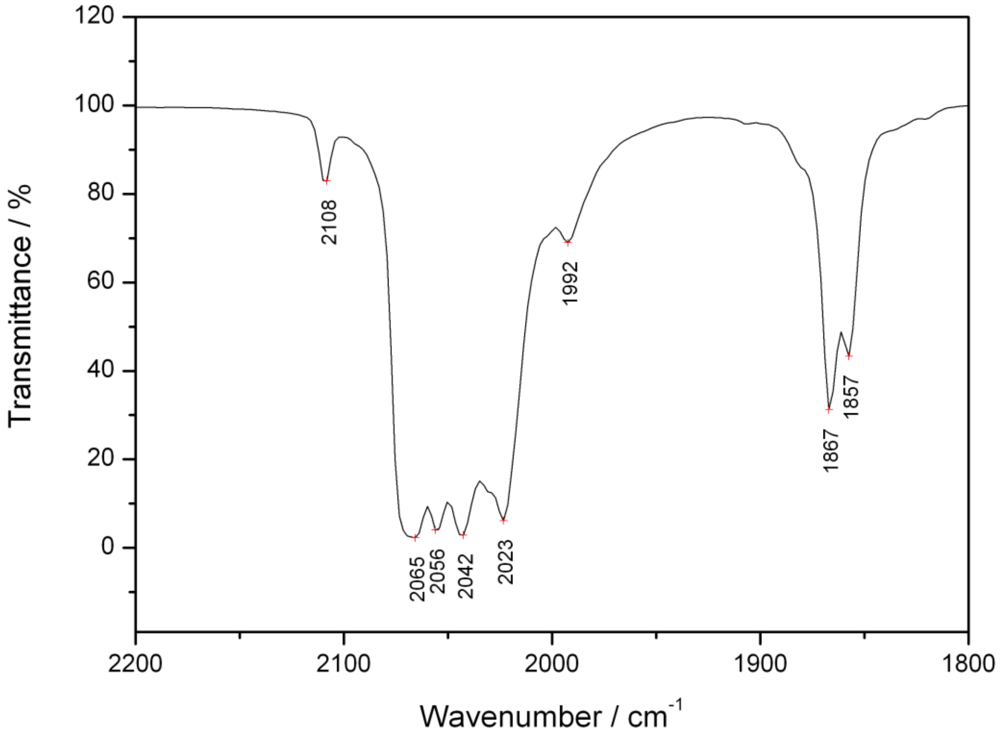

Figure S9. Section of the IR spectra of **1c** in *n*-hexane.

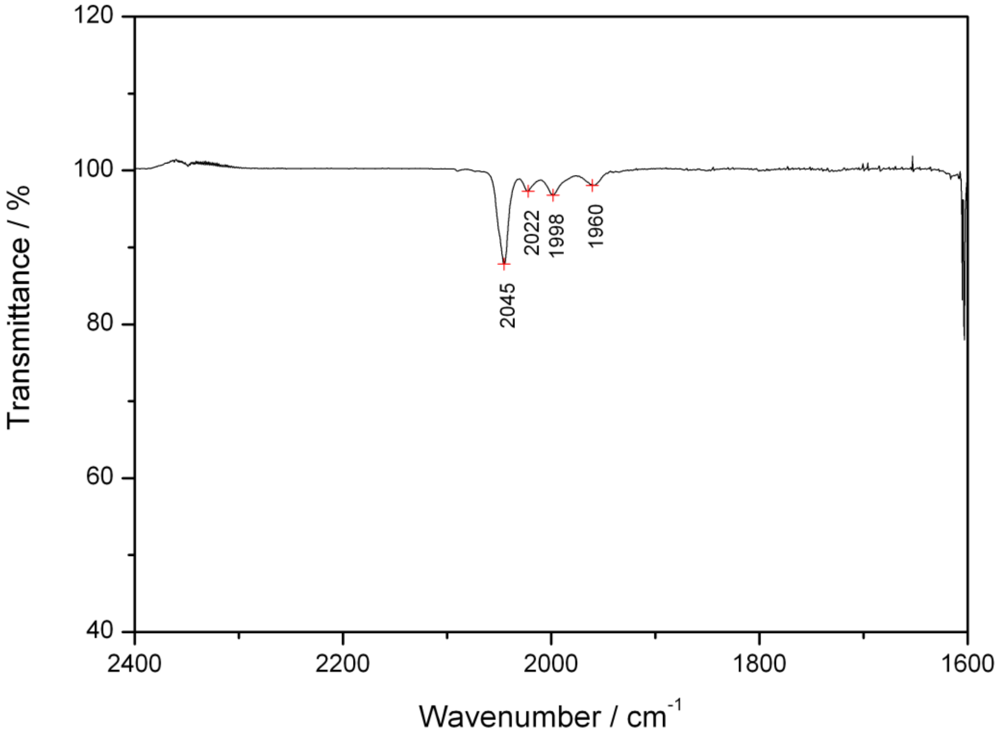

Figure S10. Section of the IR spectra of **2a** in toluene.

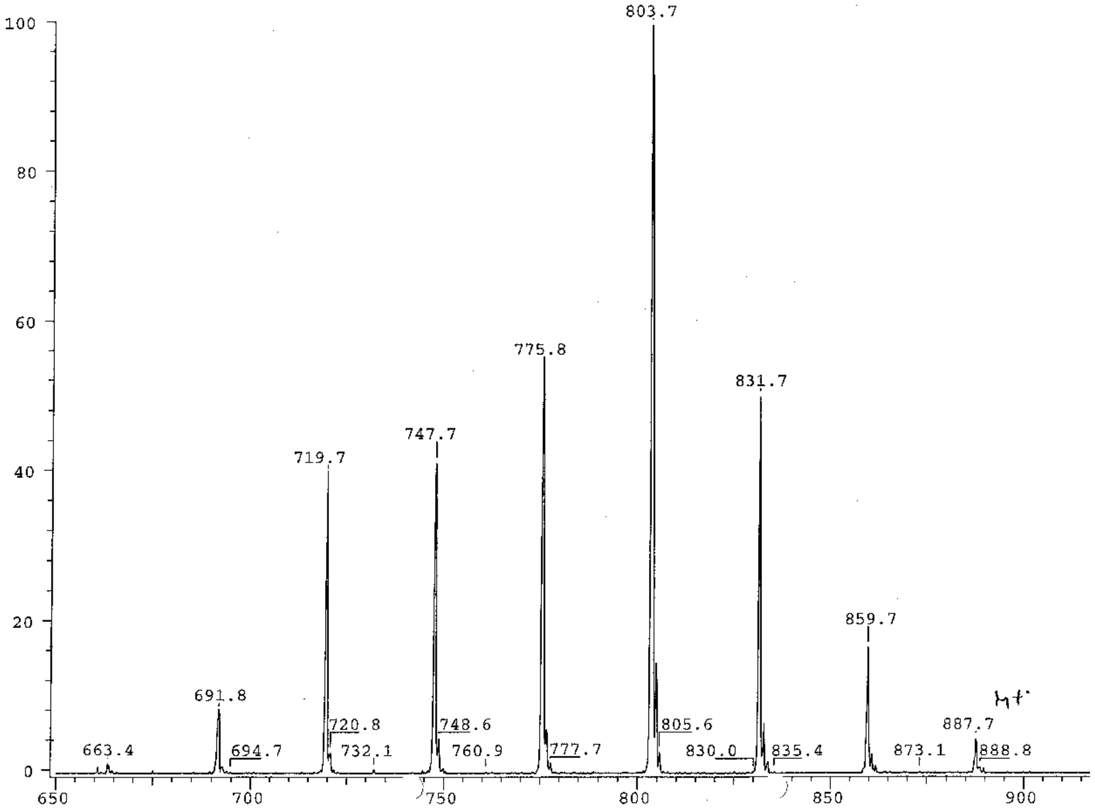

Figure S11. EI mass spectra of **1a** in *n*-hexane.

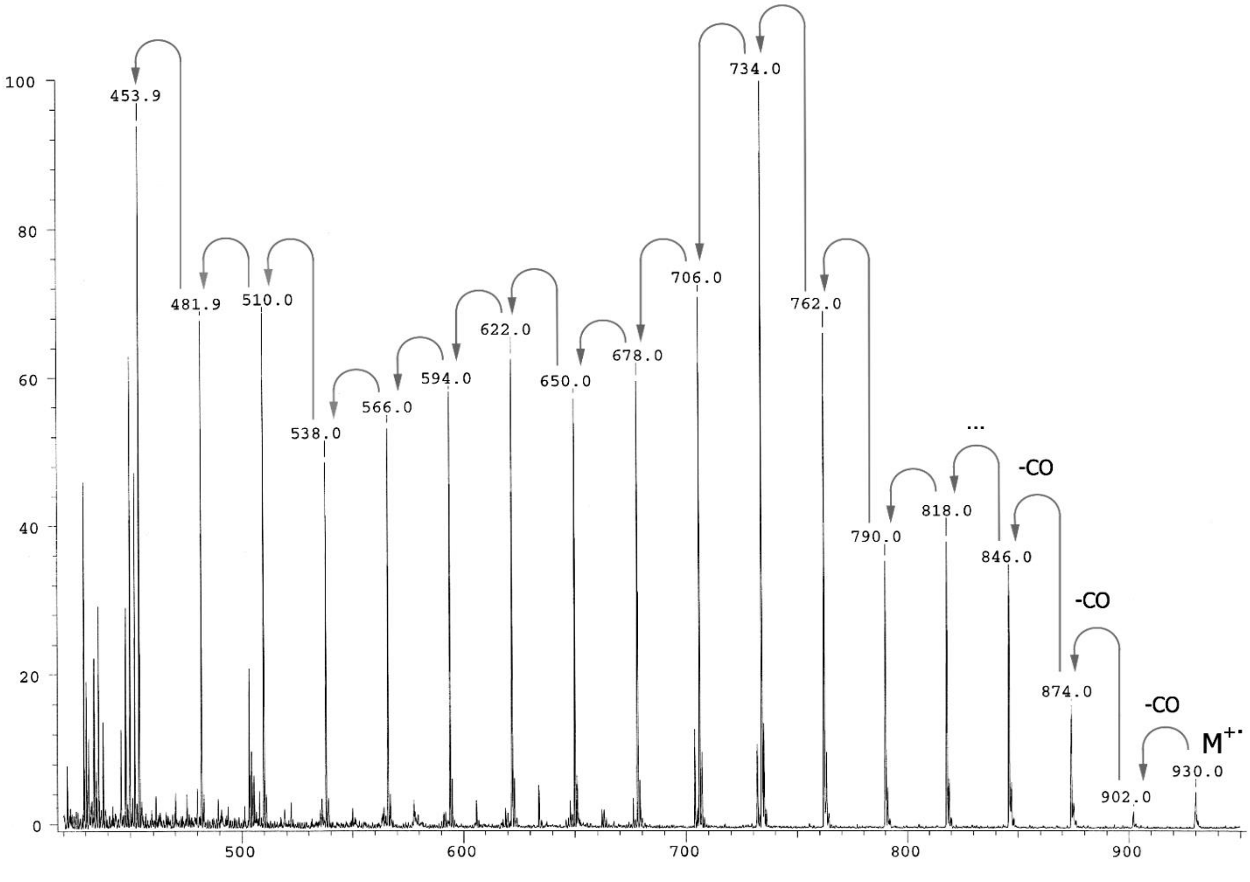

Figure S12. EI mass spectra of **1b** in *n*-hexane.

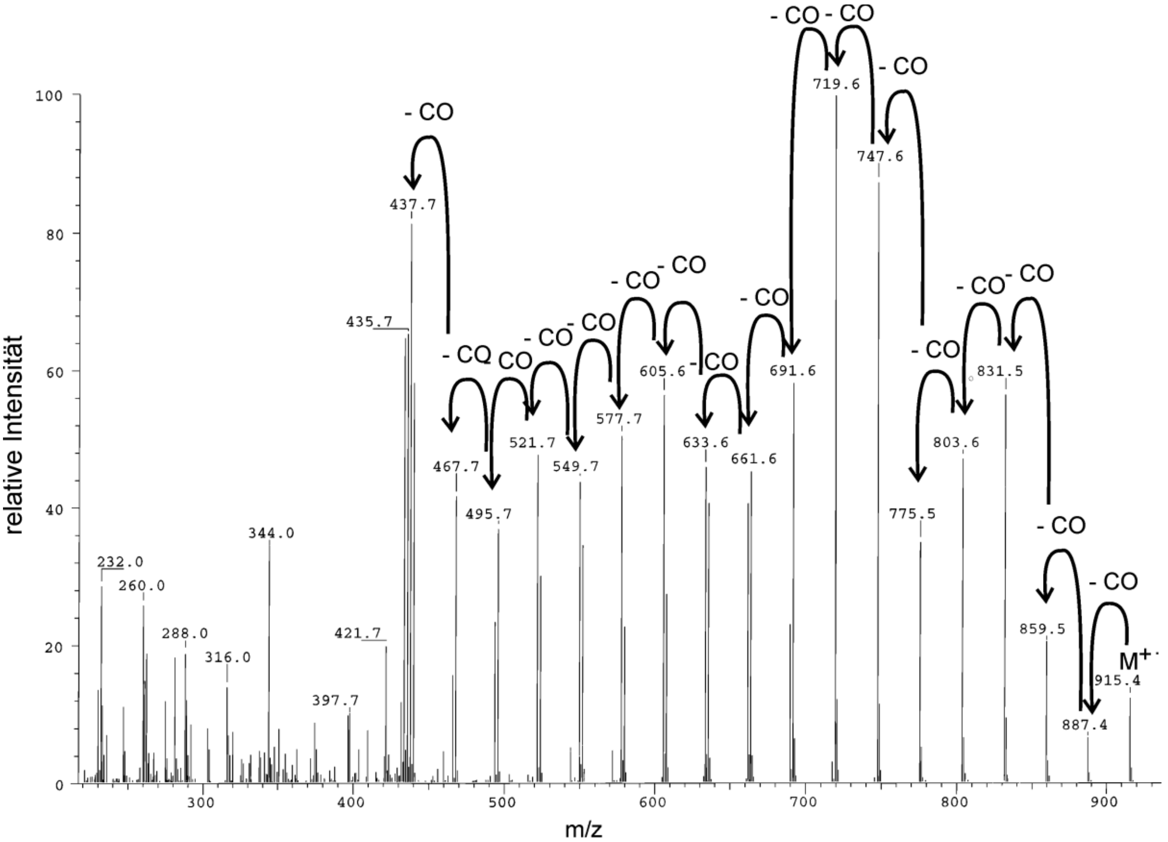

Figure S13. EI mass spectra of **1c** in hexane.

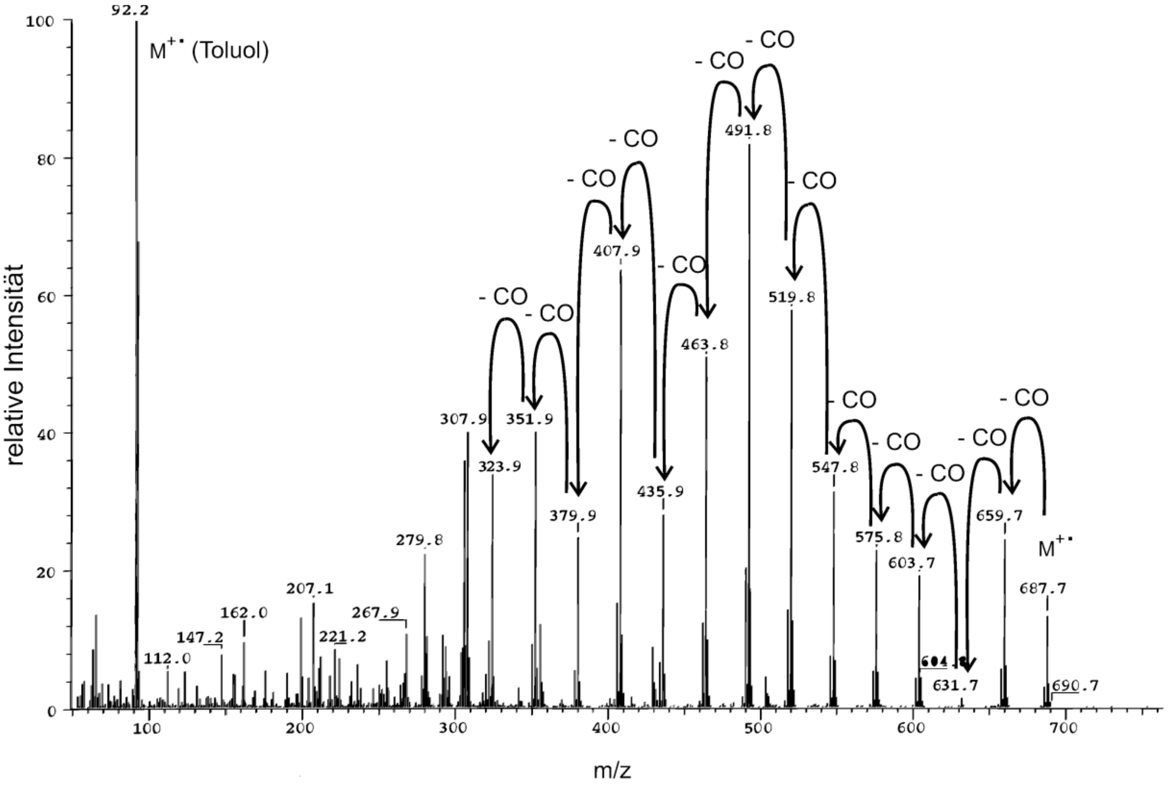

Figure S14. EI mass spectra of **2a** in toluene.

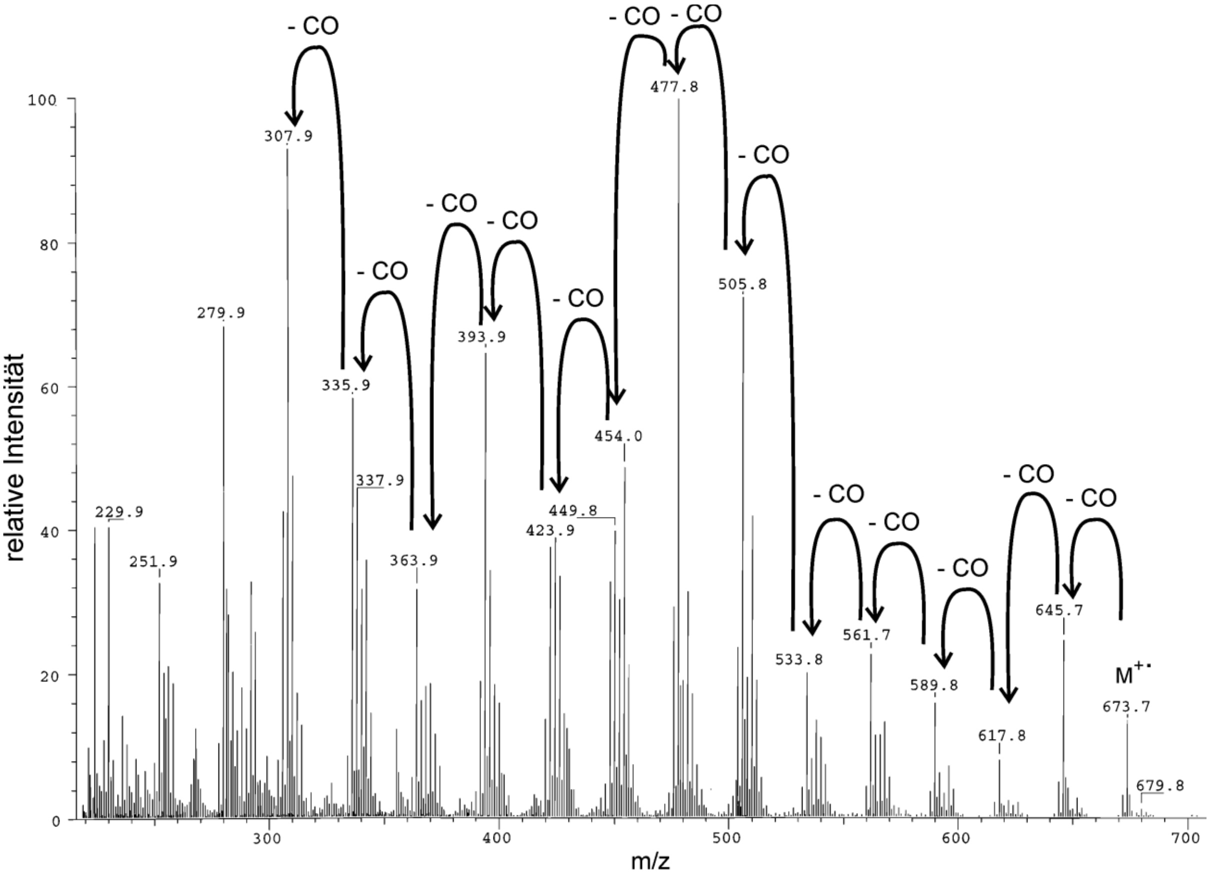

Figure S15. EI mass spectra of **2b** in hexane.

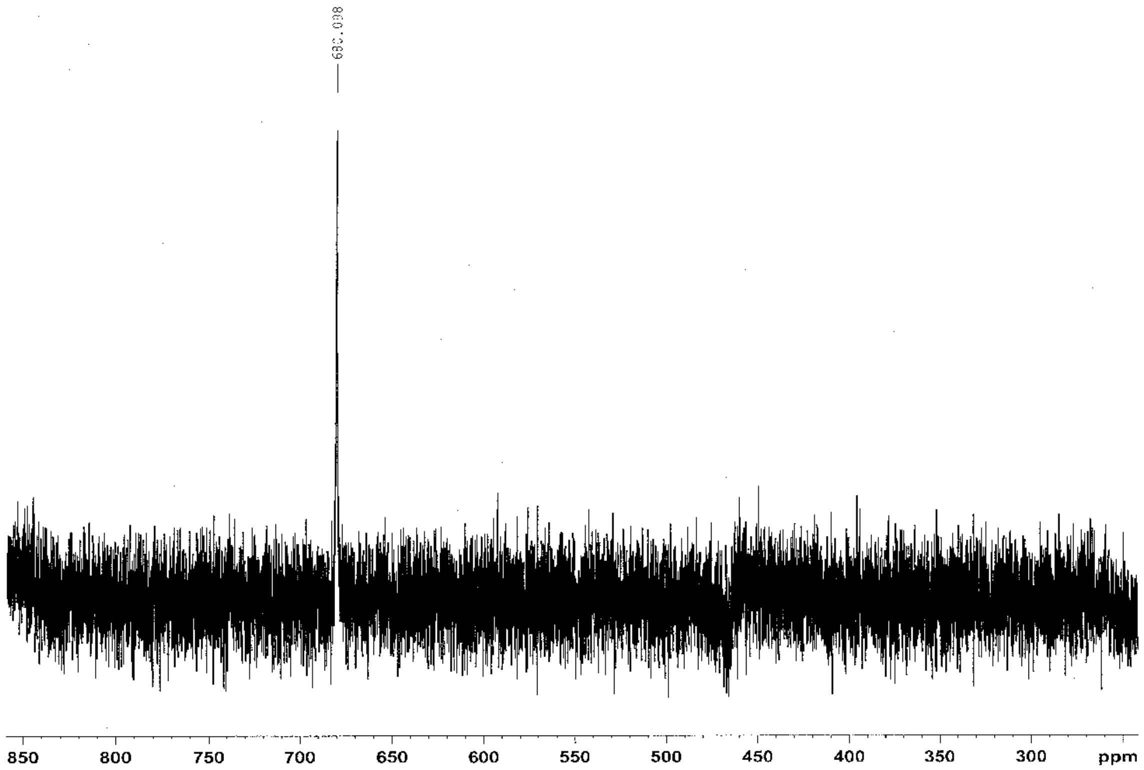

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **1a** in C_6D_6.

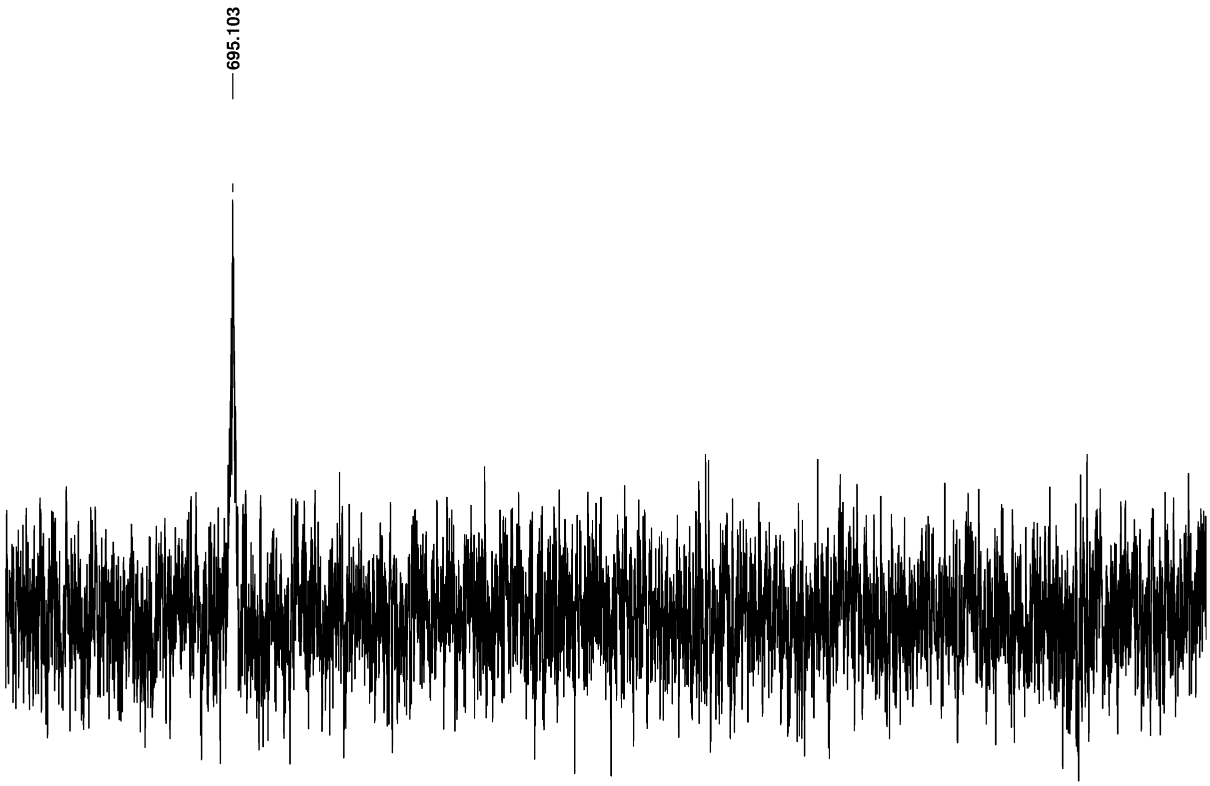

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6.

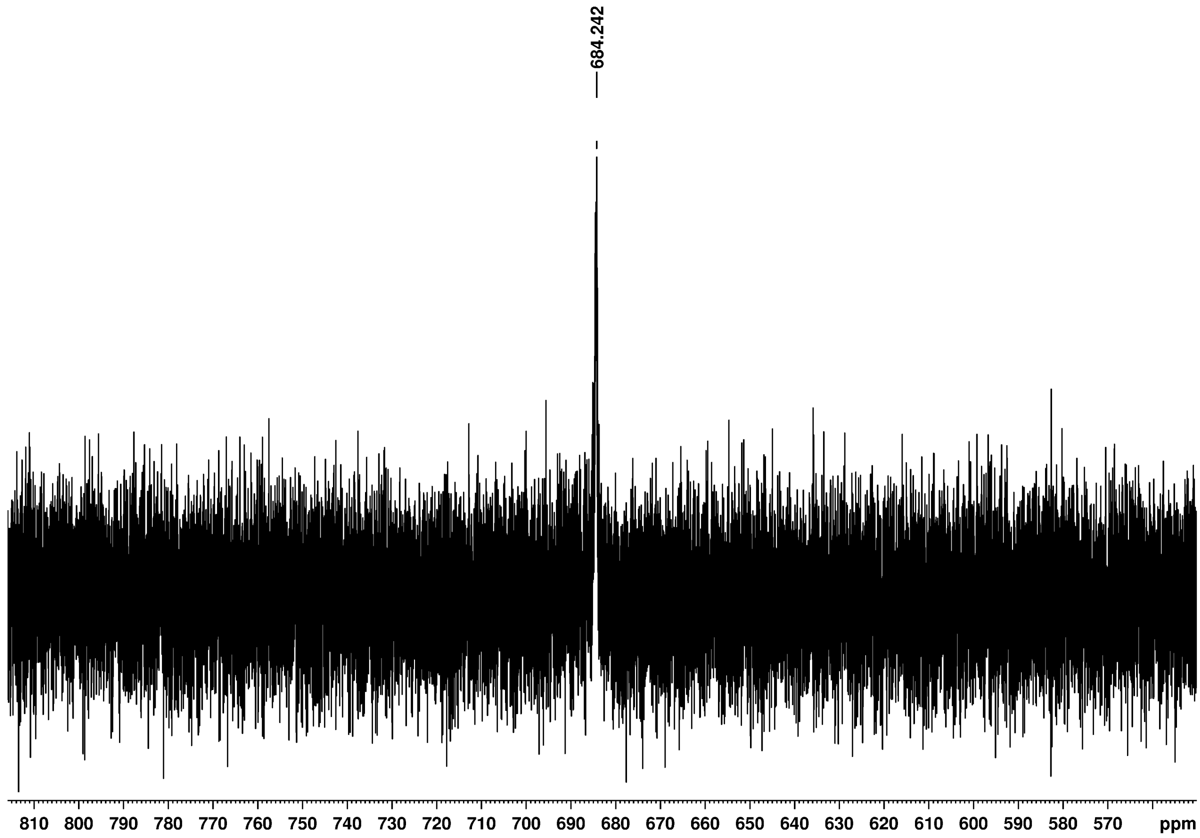

Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **1c** in C_6D_6.

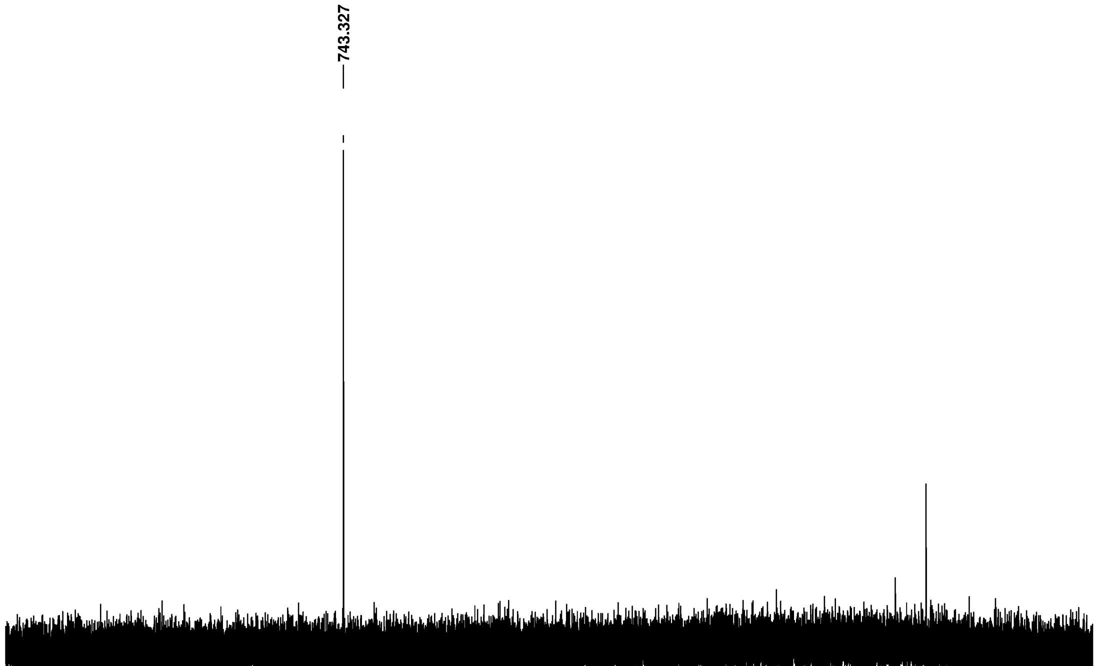

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

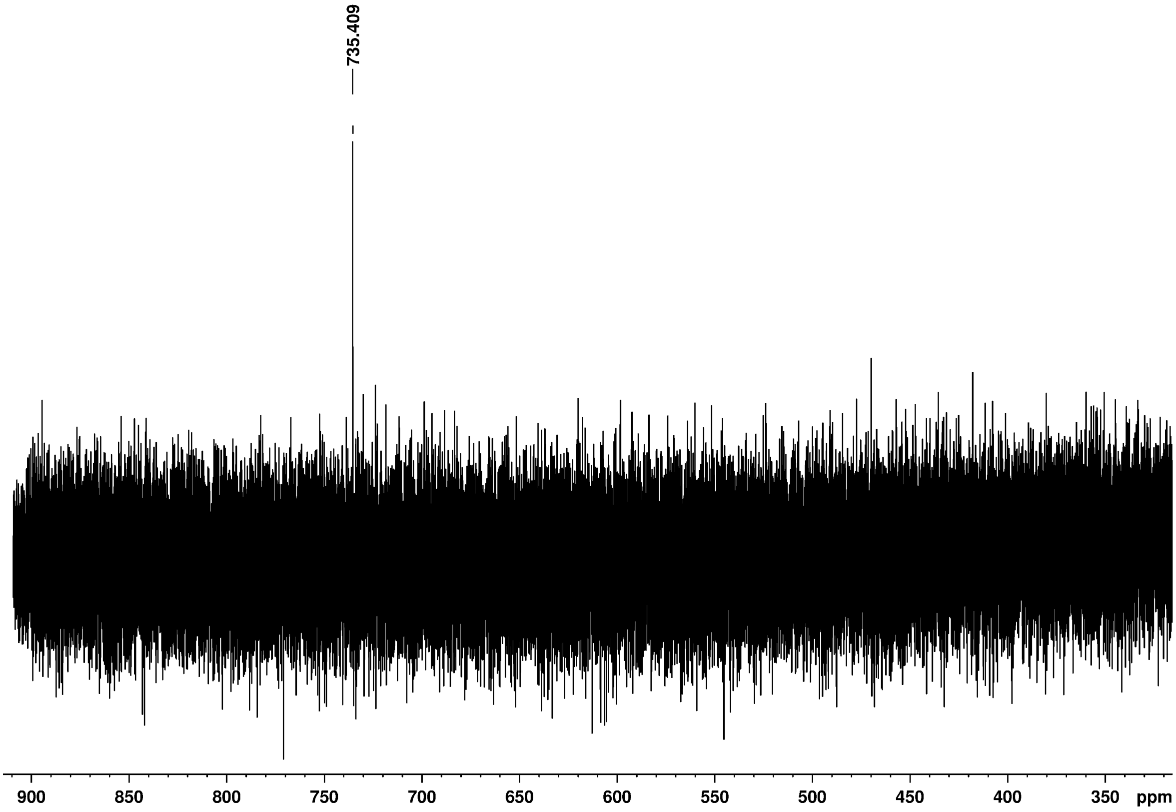

Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6.

References

[1] a) G. M. Kosolapoff, *J. Am. Chem. Soc.* **1947**, *69*, 1002-1003; b) C. Grandin, E. About-Jaudet, N. Collignon, J.-M. Denis, P. Savignac, *Heteroat. Chem* **1992**, *3*, 337-343; c) J.-C. Guillemin, T. Janati, J.-M. Denis, *J. Org. Chem.* **2001**, *66*, 7864-7868.

[2] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch., B: Chem. Sci.* **1981**, *36*, 16-19.

[3] E.-M. Rummel, M. Eckhardt, M. Bodensteiner, E. V. Peresypkina, W. Kremer, C. Gröger, M. Scheer, *Eur. J. Inorg. Chem.* **2013**, n/a-n/a.

[4] a) E. Speyer, H. Wolf, *Berichte der deutschen chemischen Gesellschaft (A and B Series)* **1927**, *60*, 1424-1425; b) D. F. Keeley, R. E. Johnson, *J. Inorg. Nucl. Chem.* **1959**, *11*, 33-41.

[5] P. Szabo, L. Marko, G. Bor, *Chem. Techn. (Berlin)* **1961**, *13*, 549.

[6] A. Technologies, *CrysAlisPro Software system, different versions* **2006-2011**, Agilent Technologies UK Ltd, Oxford, UK.

[7] R. C. Clark, J. S. Reid, *Acta Crystallogr. Sect. A* **1995**, *51*, 887-897.

[8] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786-790.

[9] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343-350.

[10] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.

[11] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.