Supporting Information for:

# A Square-Planar Osmium(II) Complex

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# Experimental Section

## Materials and Methods

All experiments were carried out using Schlenk (argon atmosphere) and glovebox (argon atmosphere) techniques. All sol-vents were dried by passing through columns packed with activated alumina. Deuterated solvents were obtained from Euriso-Top GmbH, dried over Na/K (THF, Toluene, Benzene), distilled by trap-to-trap transfer *in vacuo*, and degassed by three freeze–pump–thaw cycles, respectively. Silica gel 60 silanized was purchased from Merck KGaA and heated at 120°C *in vacuo* for 5 days prior to use. $CoCp_2$ (abcr), CN*t*Bu (Sigma-Aldrich), CO (Linde) and $[NBu_4][PF_6]$ (Sigma-Aldrich) were used as purchased. $^{H}$PNP[1], TBP[2] and $OsCl_2(PPh_3)_3$[3] were prepared according to literature procedures. Cyclic voltammograms were recorded with a Metrohm Autolab PGSTAT101 using $Ag/Ag^+$ reference-, glassy-carbon working- and Pt-wire counterelectrodes. Experimental X-band EPR spectra were recorded on a Bruker ELEXSYS-II E500 CW-EPR. The spectra were simulated by iteration of the anisotropic g-values, (super)hyperfine coupling constants, and line widths using the EPR-simulation program W95EPR developed by Prof. Dr Frank Neese. IR spectra were recorded with a Thermo Scientific Nicolet iZ10 FT/IR spectrometer at room temperature. Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL-5 SQUID magnetometer in the temperature range from 295 to 2 K at 0.5 T applied field. The powdered sample was contained in a Teflon bucket and fixed in a non-magnetic sample holder. Each raw data point for the measured magnetic moment of the sample was corrected for the diamagnetic contribution by subtraction of the experimentally determined magnetic measurement of the Teflon bucket. The molar susceptibility data were corrected for the diamagnetic contribution using the Pascal constants and the increment method according to Haberditzl.[4] Experimental data were modelled with the *julX* program.[5] Elemental analyses were obtained from the analytical laboratories at the Georg-August University on an Elementar Vario EL 3. NMR Spectra were recorded on Bruker Avance III 300, Bruker Avance III 300, Bruker Avance III 400 and Bruker Avance III HD 500 and were calibrated to the residual solvent proton resonance. ($d_6$-Benzene $\delta_H$ = 7.16 ppm, $d_8$-THF $\delta_H$ = 3.58 ppm, $d_8$-toluene $\delta_H$ = 2.08 ppm). LIFDI-spetrometry was performed on a Joel AccuTOF spectrometer under inert conditions.

**Synthesis of $[OsHCl_2\{N(CH_2CH_2PtBu_2)_2\}]$ (11):** $OsCl_2(PPh_3)_3$ (800 mg, 0.76 mmol, 1.0 eq) is dissolved in $C_6H_6$/pentane (5:1, 30 mL) and $^{H}$PNP (280 mg, 0.76 mmol, 1.0 eq) in $C_6H_6$ (5 mL) is added to the solution. The mixture is stirred for 45 min at RT. The solvent is removed and the solid is washed with pentane at 0°C (4 x 10 mL). DCM (15 mL) is added to the solid and the solution is heated to 40°C for 16h. The solvent is removed and the crude product is purified by washing with $Et_2O$ (4 x 10 mL) and EtOH (4 x 5 mL). The solid is extracted with DCM (5 x 2 mL) and the solvent is removed. $[OsHCl_2\{N(CH_2CH_2PtBu_2)_2\}]$ (358 mg, 0.57 mmol, 75%) is isolated in form of a green solid. Spectroscopic characterization data was identical with the prior reported values.[6]

**Synthesis of $[OsCl_2\{N(CHCHPtBu_2)_2\}]$ (12):** $[OsHCl_2\{N(CH_2CH_2PtBu_2)_2\}]$ (160 mg, 0.26 mmol, 1.0 eq) and TBP (370 mg, 1.41 mmol, 7.0 eq) are dissolved in PhCl (20 mL) and stirred at 50°C for 4.5 h. The solvent is removed and the residue is washed with pentanes (8 x 10 mL) and extracted with benzene (5 x 5 mL). Lyophilization yields $[OsCl_2\{N(CHCHPtBu_2)_2\}]$ as a dark green powder (149 mg, 0.24 mmol, 95 %). Anal. Calcd for $C_{20}H_{40}Cl_2N_1Os_1P_2$ (617.62): C, 38.9; H, 6.53; N, 2.27 Found: C, 39.4; H, 6.36; N, 2.15. NMR ($d_6$-benzene): $^1$H (300 MHz, RT): $\delta$ = 43.9 (br, 2H, C*H*), -0.06 (br, 36H, P(C(C*H*$_3$)$_2$), -97.7 (br, 2H, C*H*). MS (LIFDI, toluene): *m/z* = 618.0 (100%, [M$^+$]). $\mu_{eff}^{297\,K}$ = 1.65 $\mu_B$.

**Synthesis of $[OsCl\{N(CHCHPtBu_2)_2\}]$ (13):** $[OsCl_2\{N(CHCHPtBu_2)_2\}]$ (20.0 mg, 32.4 µmol, 1.0 eq) and $CoCp_2$ (6.1 mg, 32.4 µmol, 1.0 eq) are dissolved in THF (2 mL) at -35°C and stirred for 1 min. The solvent is removed and the residue is extracted with pentane. Crystallization at -35°C yields $[OsCl\{N(CHCHPtBu_2)_2\}]$ in form of dark purple crystals which are suitable for SQUID measurements (10.0 mg, 17.2 µmol, 53%). *Combustion analysis could not be obtained due to decomposition during drying in vacuo, presumably from loss of isobutene (see Figure 11). However, SQUID data was reproduced with 3 independent samples.* NMR ($d_6$-Benzene): $^1$H (300 MHz, RT): $\delta$ = 18.42 (ABXX'B'A', $N = |^3J_{AX} + {}^4J_{AX'}|$ = 17.0 Hz, $^3J_{AB}$ = 6.0 Hz. 2H, NC*H*), -4.20 ($A_{18}XX'A'_{18}$, $N = |^3J_{AX} + {}^5J_{AX'}|$ = 6.0 Hz, 36H, P(C(C*H*$_3$)$_2$), -35.28 (d, $^3J_{AB}$ = 6.1 Hz, 2H, PC*H*). $^{13}$C (125.76 MHz): $\delta$ = 262.4 (d, $^1J_{CH}$ = 165.1 Hz, 2C, P*C*H), 77.1 (q, $^1J_{CH}$ = 125.5, 12C, P(C(*C*H$_3$)$_3$)$_2$), 34.3 (br, 4C, P(*C*(CH$_3$)$_3$)$_2$), 31.4 (d, $^1J_{CH}$ = 162.3 Hz, 2C, N*C*H). $^{31}$P{$^1$H} (161.25 MHz): $\delta$ = -978.2 (s, 2P, *P*(C(CH$_3$)$_3$)$_2$). MS (LIFDI, toluene): *m/z* = 583.1 (100%, [M$^+$]).

Synthesis of [OsCl{N(CHCHP*t*Bu$_2$)$_2$}(CN*t*Bu)] (14): [OsCl$_2${N(CHCHP*t*Bu$_2$)$_2$}] (25.0 mg, 40.5 µmol, 1.0 eq) and CoCp$_2$ (7.7 mg, 42.3 µmol, 1.0 eq) are dissolved in benzene (5 mL) and stirred for 1 min. CN*t*Bu (4.6 µL, 40.5 µmol, 1.0 eq) is added and the solution is stirred for an additional minute. After filtration the crude product is purified *via* column chromatography with silanized silica (benzene). Lyophilization yields [OsCl{N(CHCHP*t*Bu$_2$)$_2$}(CN*t*Bu)] as a purple powder (18.3 mg, 27.5 µmol, 68%). Anal. Calcd for $C_{25}H_{49}Cl_1N_2Os_1P_2$ (665.30): C, 45.1; H, 7.42; N, 4.21 Found: C, 45.4; H, 8.02; N, 4.10. NMR ($d_6$-benzene, RT): $^1$H (400 MHz): $\delta$ = 7.04 (ABXX'B'A', $N = |^3J_{AX} + {}^4J_{AX'}|$ = 17.0 Hz, $^3J_{AB}$ = 5.9 Hz. 2H, NC*H*), 4.33 (ABXX'B'A', $N = |^2J_{AX}+{}^4J_{AX'}|$ = 2.6 Hz, $^3J_{AB}$ = 5.9 Hz, 2H, PC*H*), 1.51 ($A_9XX'A'_9$, $N = |^3J_{AX} + {}^5J_{AX'}|$ = 6.6 Hz, 18H, P(C(C*H*$_3$)$_3$)), 1.22 ($A_9XX'A'_9$, $N = |^3J_{AX} + {}^5J_{AX'}|$ = 6.6 Hz, 18H, P(C(C*H*$_3$)$_3$)), 1.19 (s, 9H, CN(C(C*H*$_3$)$_3$)). $^{13}$C{$^1$H} (125.76 MHz): $\delta$ = 166.8 (AXX'A', $N = |^2J_{AX} + {}^3J_{AX'}|$ = 3.6 Hz, 2C, N*C*H), 89.2 (AXX'A', $N = |^1J_{AX} + {}^3J_{AX'}|$ = 23.5 Hz, 2C, PC*H*), 58.0 (s, 1C, CN(*C*(CH$_3$)$_3$), 39.3 (AXX'A', $N = |^1J_{AX} + {}^3J_{AX'}|$ = 11.2 Hz, 2C, P(*C*(CH$_3$)$_3$), 36.3 (AXX'A', $N = |^1J_{AX} + {}^3J_{AX'}|$ = 11.8 Hz, 2C, P(*C*(CH$_3$)$_3$), 33.3 (s, 3C, CN(*C*H$_3$)$_3$), 30.7 ($A_3XX'A'_3$, $N = |^2J_{AX} + {}^4J_{AX'}|$ = 2.7 Hz, 6C, P(C(*C*H$_3$)$_3$), 28.9 ($A_3XX'A'_3$, $N = |^2J_{AX} + {}^4J_{AX'}|$ = 2.7 Hz, 6C, P(C(*C*H$_3$)$_3$). *The isonitrile C≡N resonance was not detected.* $^{31}$P{$^1$H} (161.25 MHz): $\delta$ = 55.6 (s, 2P, *P*(C(CH$_3$)$_3$)$_2$). MS (LIFDI, toluene): *m/z* = 666.2 (100%, [M$^+$]). IR (KBr): $\tilde{\nu}$ = 1931 (C=N).

Synthesis of [OsCl{N(CHCHP*t*Bu$_2$)$_2$}(CO)] (15): [OsCl$_2${N(CHCHP*t*Bu$_2$)$_2$}] (15.0 mg, 24.3 µmol, 1.0 eq) and CoCp$_2$ (4.6 mg, 24.3 µmol, 1.0 eq) are dissolved in THF (10 mL) in a 50 mL J-Young flask and stirred for 1 min at room temperature. The solution is degassed with three successive freeze-pump-thaw cycles and allowed to warm to room temperature. Upon melting, CO (600 µL, 1bar, 24.3 µmol, 1.0 eq) is slowly bubbled through the solution. The solution is stirred for 10 min at room temperature. After removal of the solvent the crude product is washed with pentanes (1 x 1 mL) and extracted with benzene (3 x 0.5 mL). The solution is concentrated and the product is further purified *via* column chromatography with silanized silica (benzene). The solvent is removed and the product is crystallized from Et$_2$O at -35°C. The crystals are washed with pentanes and dried. Lyophilization yields [OsCl{N(CHCHP*t*Bu$_2$)$_2$}(CO)] (9.5 mg, 15.6 µmol, 64 %) as a purple powder. Anal. Calcd for $C_{21}H_{40}N_1O_1OsP_2$ (610.18): C, 41.3; H, 6.61; N, 2.30; Found: C, 41.0; H, 6.21; N, 2.12. NMR ($d_6$-benzene): $^1$H (400 MHz): $\delta$ = 6.92 (ABXX'B'A', $N = |^3J_{AX} + {}^4J_{AX'}|$ = 20.1 Hz, $^3J_{AB}$ = 5.8 Hz, 2H, NC*H*), 4.30 (ABXX'B'A', $N = |^2J_{AX}+{}^4J_{AX'}|$ = 2.8 Hz, $^3J_{AB}$ = 5.8 Hz, 2H, PC*H*), 1.41 ($A_9XX'A'_9$, $N = |^3J_{AX} + {}^5J_{AX'}|$ = 7.3 Hz, 18H, P(C(C*H*$_3$)$_3$)), 1.16 ($A_9XX'A'_9$, $N = |^3J_{AX} + {}^5J_{AX'}|$ = 6.8 Hz, 18H, P(C(C*H*$_3$)$_3$)). $^{13}$C{$^1$H} (125.76 MHz): $\delta$ = 168.4 (t, $^2J_{CP}$ = 7.9 Hz, 1 C, *C*O), 166.8 (AXX'A', $N = |^2J_{AX} + {}^3J_{AX'}|$ = 6.6 Hz, 2C, N*C*H), 89.7 (AXX'A', $N = |^1J_{AX} + {}^3J_{AX'}|$ = 21.7 Hz, 2C, PC*H*), 39.2 (AXX'A', $N = |^1J_{AX} + {}^3J_{AX'}|$ = 11.8 Hz, 2C, P(*C*(CH$_3$)$_3$), 37.0 (AXX'A', $N = |^1J_{AX} + {}^3J_{AX'}|$ = 12.4 Hz, 2C, P(*C*(CH$_3$)$_3$), 30.0 ($A_3XX'A'_3$, $N = |^2J_{AX} + {}^4J_{AX'}|$ = 2.3 Hz, 6C, P(C(*C*H$_3$)$_3$), 28.6 ($A_3XX'A'_3$, $N = |^2J_{AX} + {}^4J_{AX'}|$ = 2.7 Hz, 6C, P(C(*C*H$_3$)$_3$). $^{31}$P{$^1$H} (161.25 MHz): $\delta$ = 65.1 (s, 2P, *P*(C(CH$_3$)$_3$)$_2$). IR (Nujol): $\tilde{\nu}$ = 1893 (C=O).

# Analytical Data for compound 12

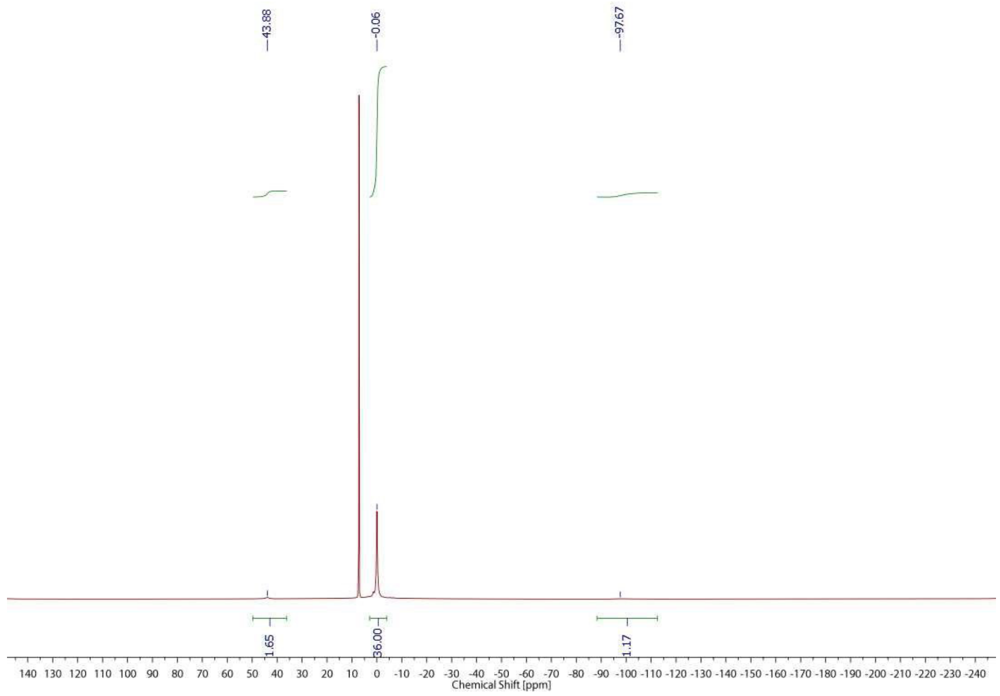



**Figure 1:** [1]H-NMR spectrum of **12**, $C_6D_6$, RT.

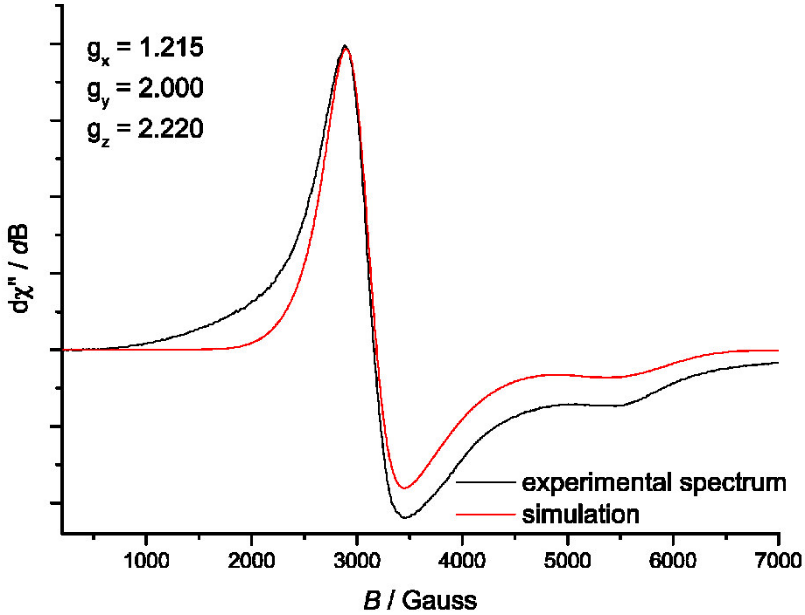



**Figure 2:** EPR-powder spectrum of **12**, 140 K, Freq.: 9.448 GHz, Mod.: 7.00 G, Power: 10 mW.

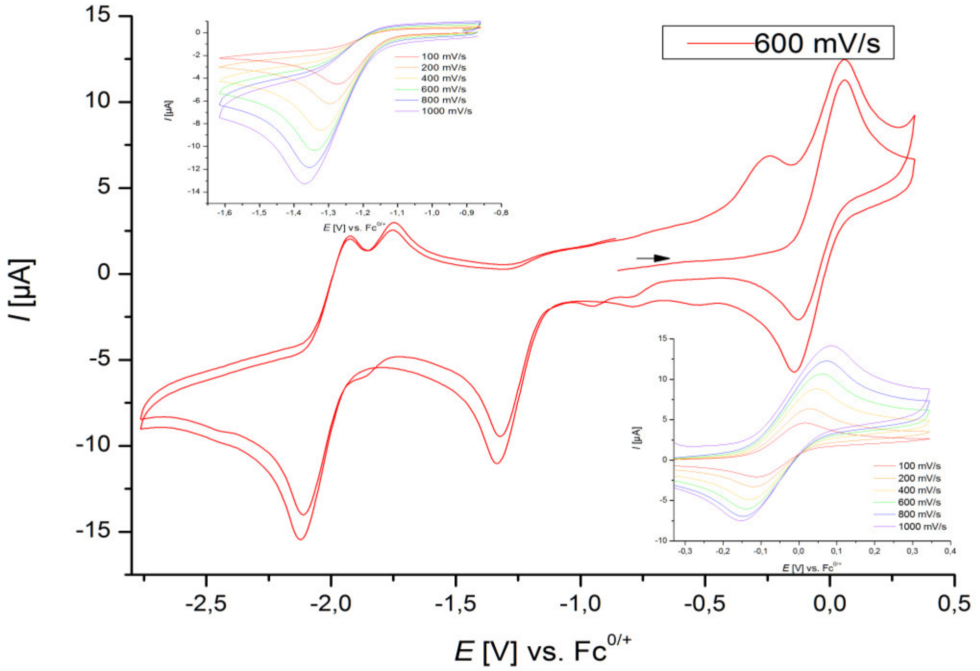



**Figure 3:** Cyclovoltammogram of **12**, THF, 0.1 M TBAHP, 0.1 mM, RT.

## Analytical Data for compound 13

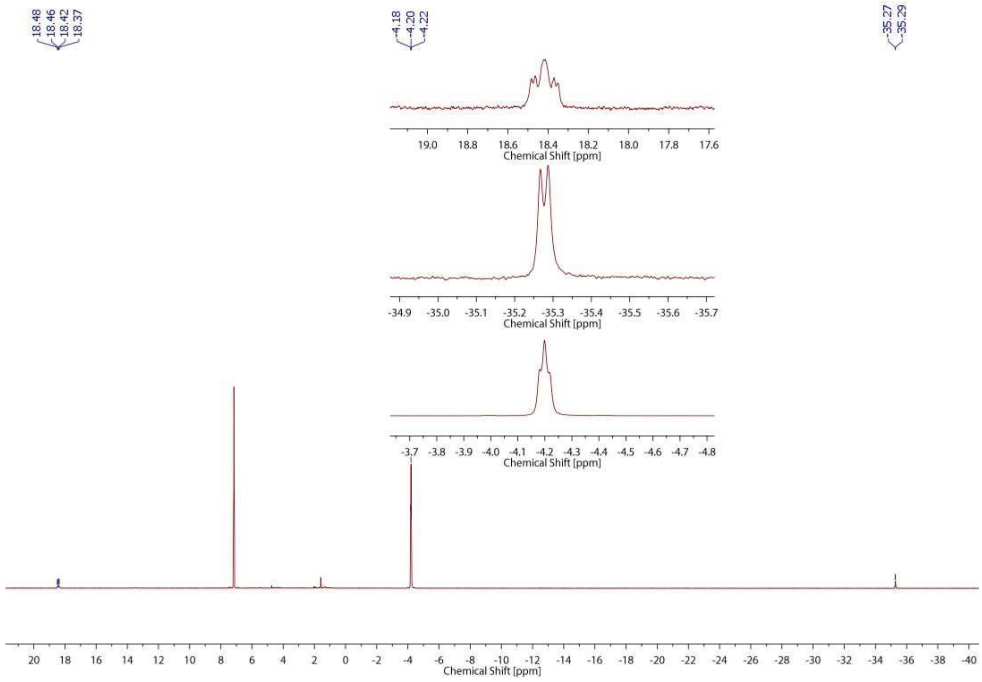


**Figure 4:** $^{1}$H-NMR spectrum of **13**, $C_6D_6$, RT.

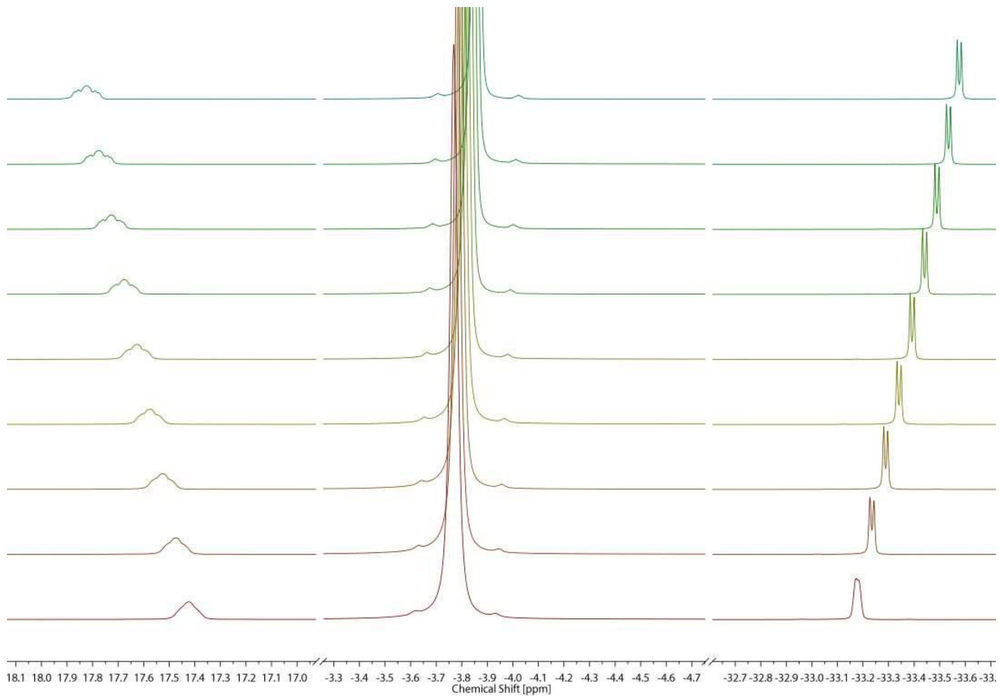


**Figure 5:** VT-$^{1}$H-NMR spectrum of **13**, Toluene-$d_8$, -55°C (red) to -15°C (green), 5°C steps.

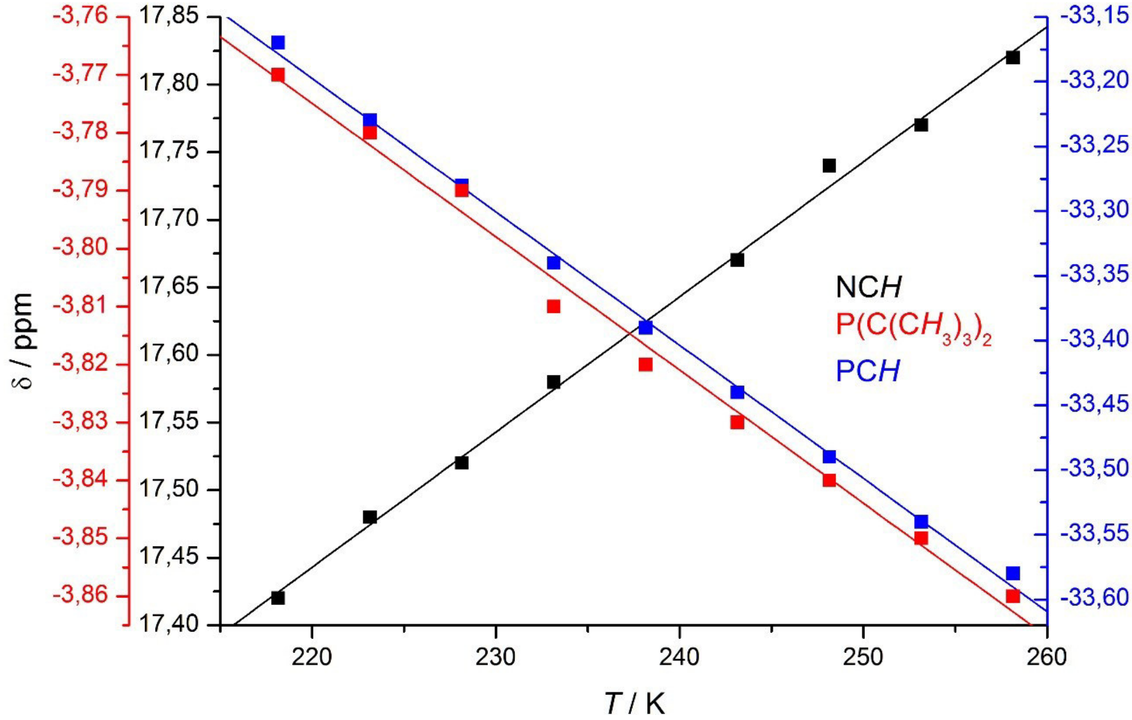



**Figure 6:** Temperature dependence of the [1]H-NMR signals of **13**.

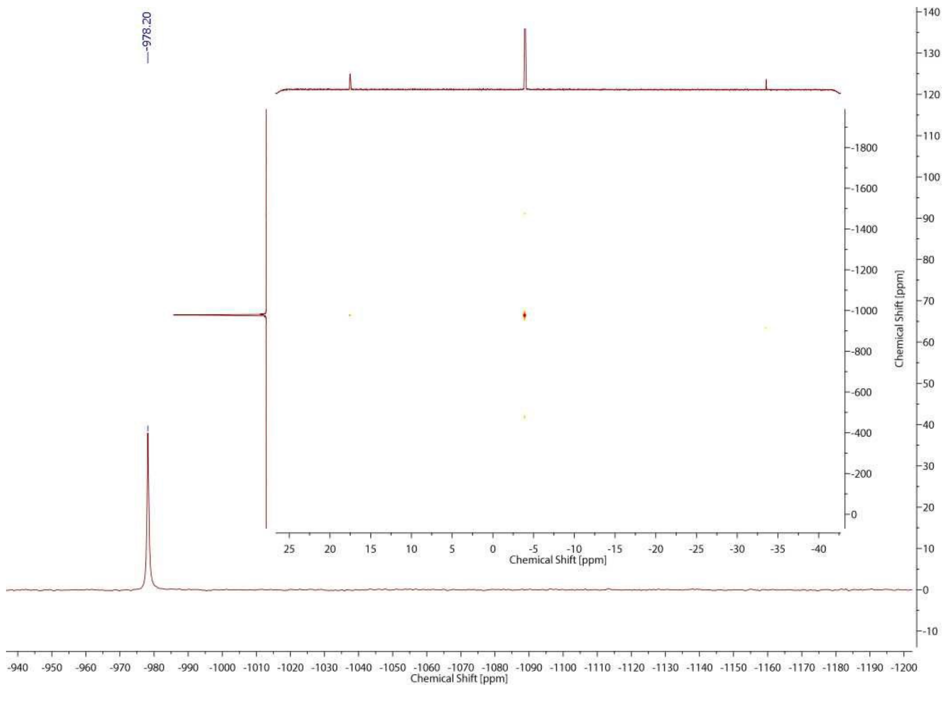



**Figure 7:** $^{31}P\{^1H\}$-NMR spectrum of **13**, $C_6D_6$, RT (inset: $^{31}P\{^1H\}$-$^1H$ HMQC NMR spectrum of **13**, Toluene-$d_8$, -35°C).

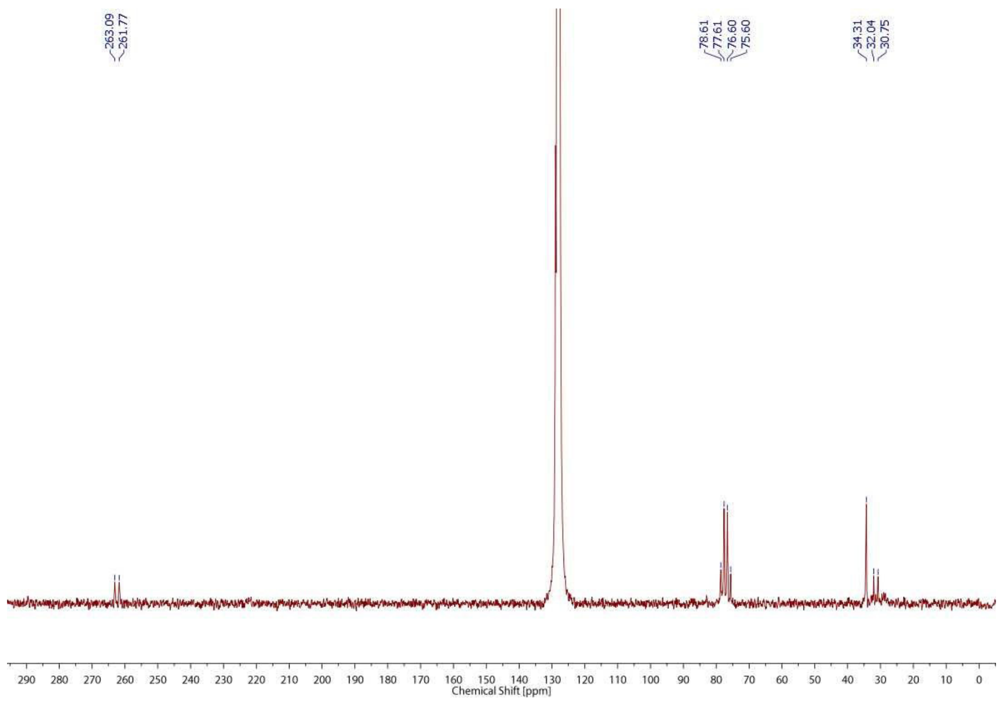



**Figure 8:** $^{13}C$-NMR spectrum of **13**, $C_6D_6$, RT.

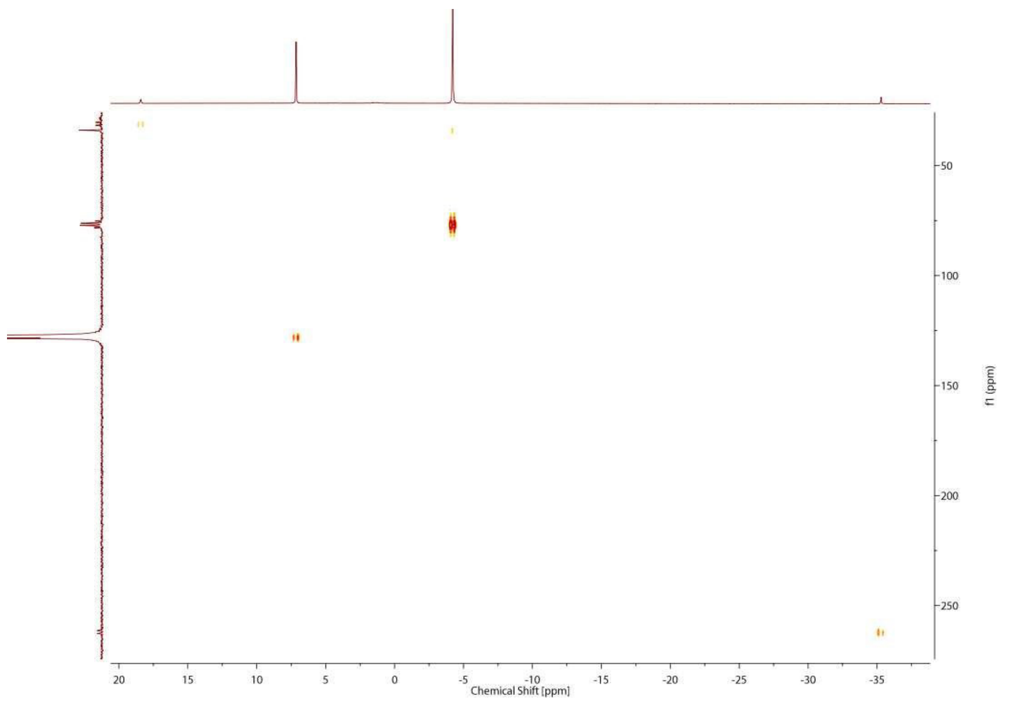



**Figure 9:** $^{13}C\{^1H\}$-$^1H$-HMQC NMR spectrum of **13**, $C_6D_6$, RT.

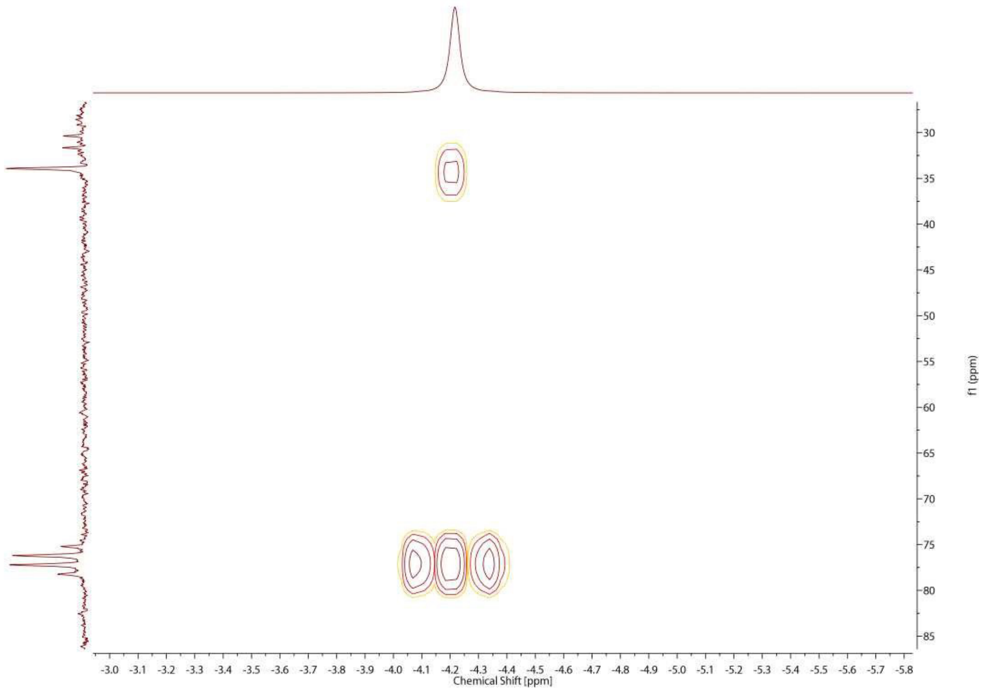


**Figure 10:** $^{13}C\{^{1}H\}$-$^{1}H$-HMBC NMR spectrum of **13**, $C_6D_6$, RT.

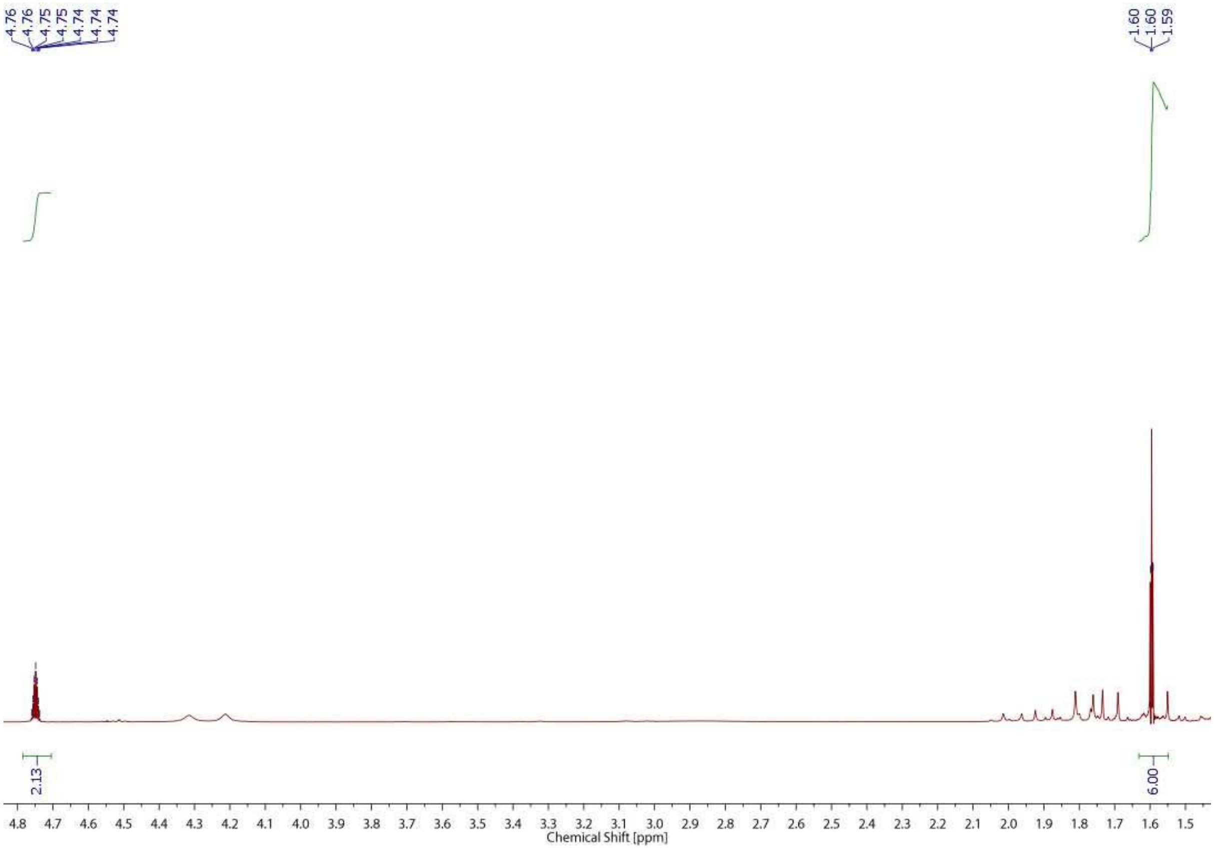


**Figure 11:** $^{1}H$ NMR spectrum of **13** after 24h at room temperature showing formation of isobutene, $C_6D_6$, RT.

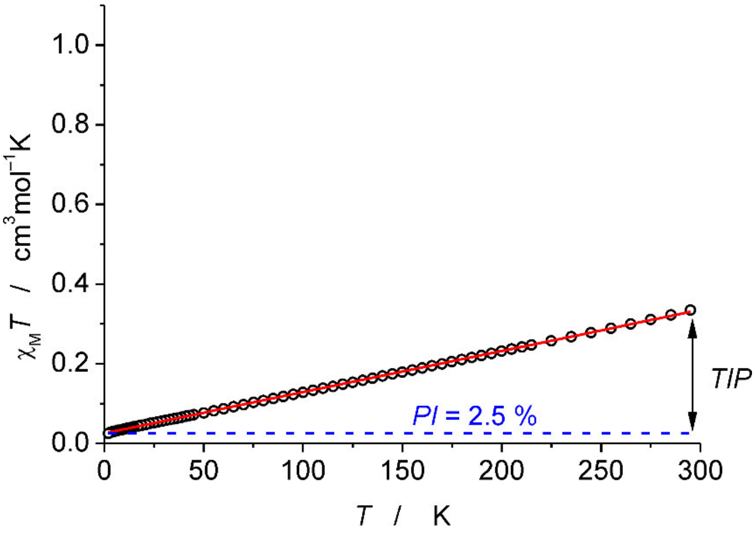



**Figure 12**: $\chi_M T$ vs. $T$ plot for **13**. The open circles are the observed susceptibility, the red solid line corresponds to the best fit with the parameters $PI$ = 2.5 % ($S$ = 1, the blue broken line, PI: paramagnetic impurity) and $TIP$ = $1030 \cdot 10^{-6}$ $cm^3 \cdot mol^{-1}$.

# Analytical Data for compound 14

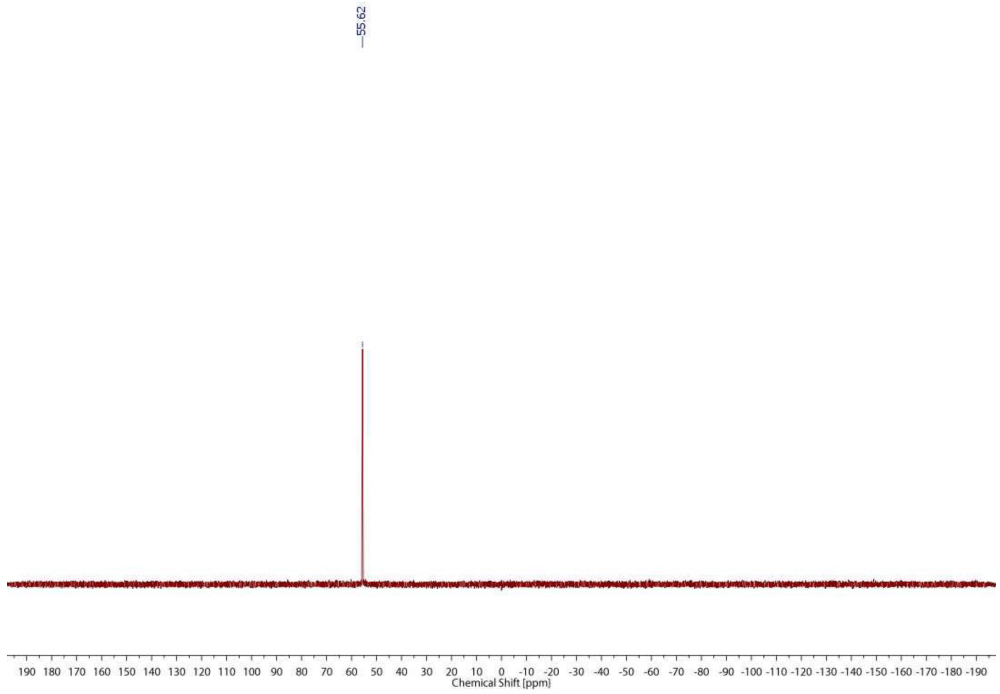



**Figure 13:** $^{31}P\{^{1}H\}$-NMR spectrum of **14**, $C_6D_6$, RT.

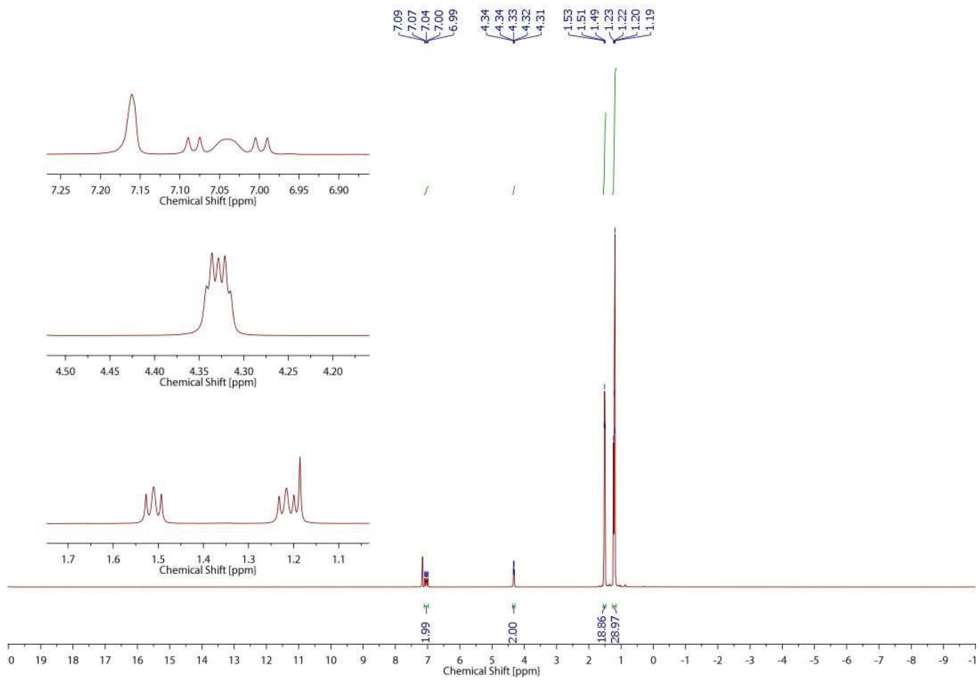



**Figure 14:** $^{1}H$-NMR spectrum of **14**, $C_6D_6$, RT.

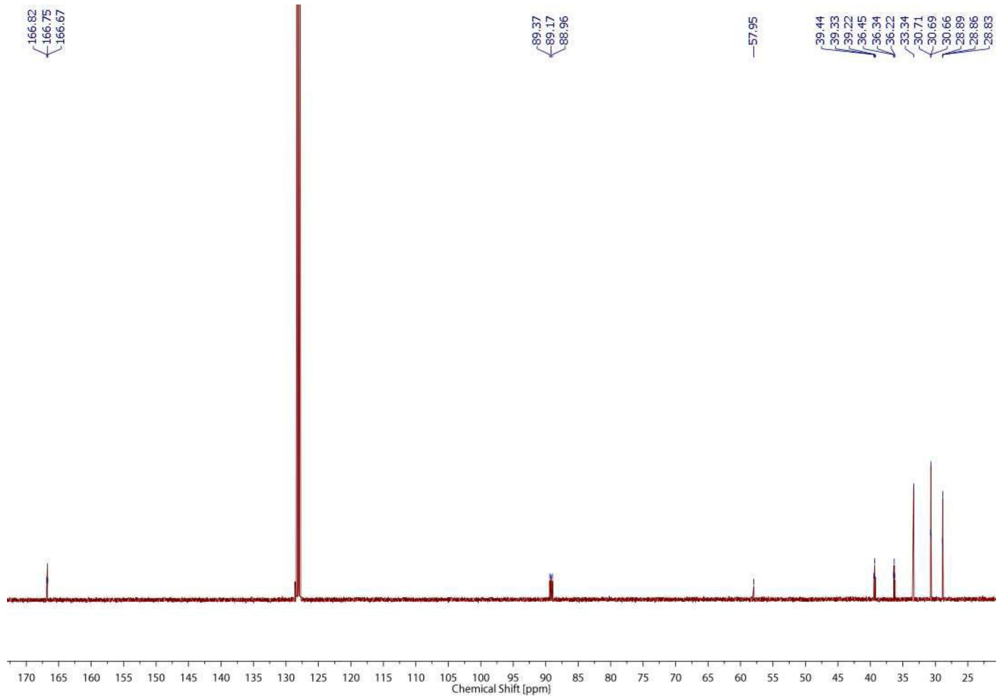



**Figure 15:** $^{13}C\{^{1}H\}$-NMR spectrum of **14**, $C_6D_6$, RT.

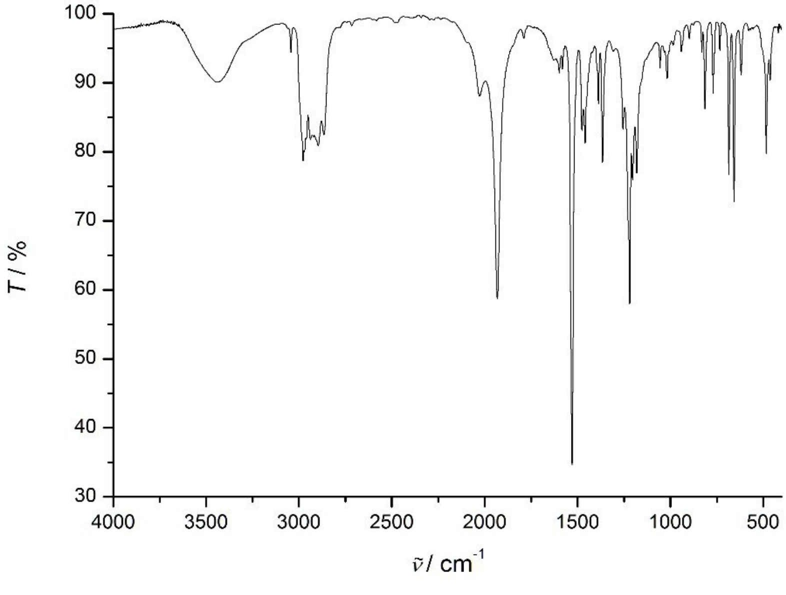



**Figure 16:** IR-Spectrum of **14**, KBr, RT.

## Analytical Data for compound 15

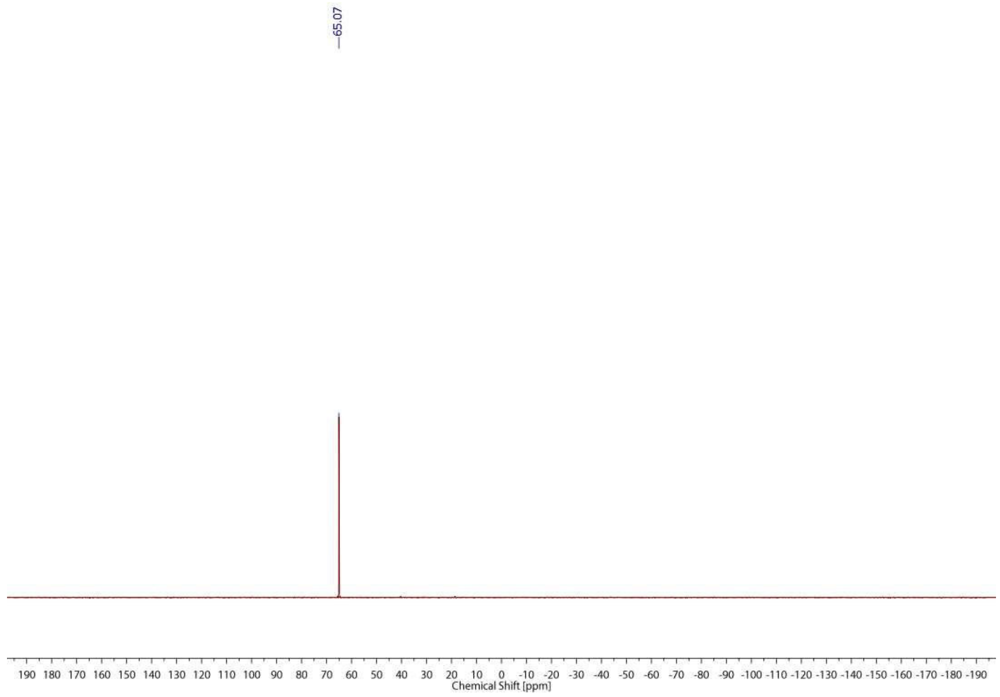



**Figure 17:** $^{31}P\{^{1}H\}$-NMR spectrum of **15**, $C_6D_6$, RT.

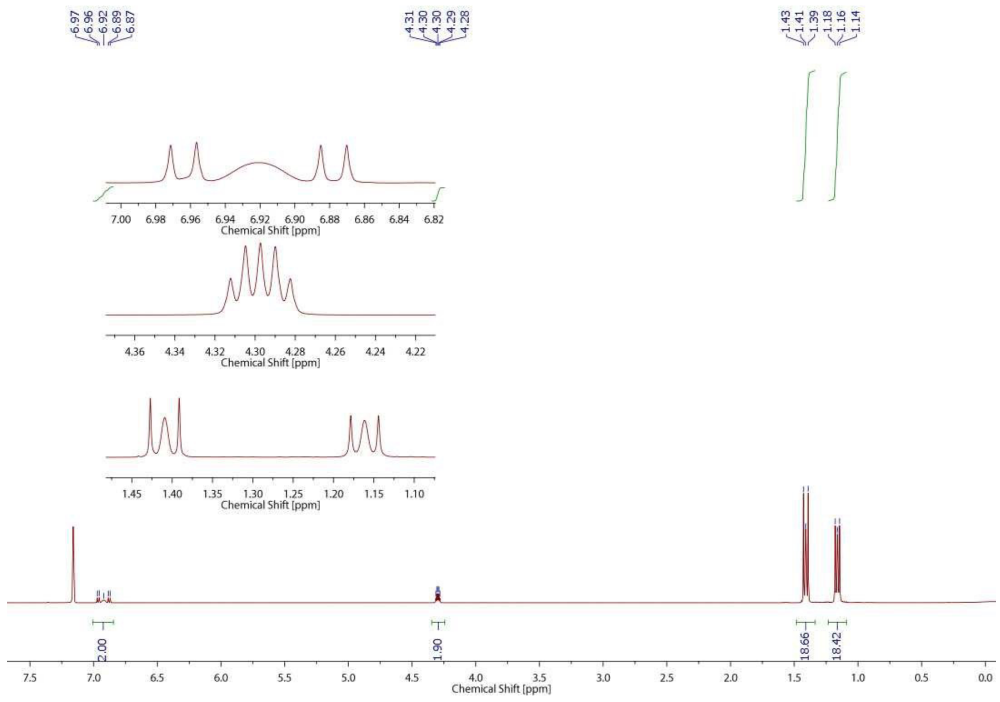



**Figure 18:** $^{1}H$-NMR spectrum of **15**, $C_6D_6$, RT.

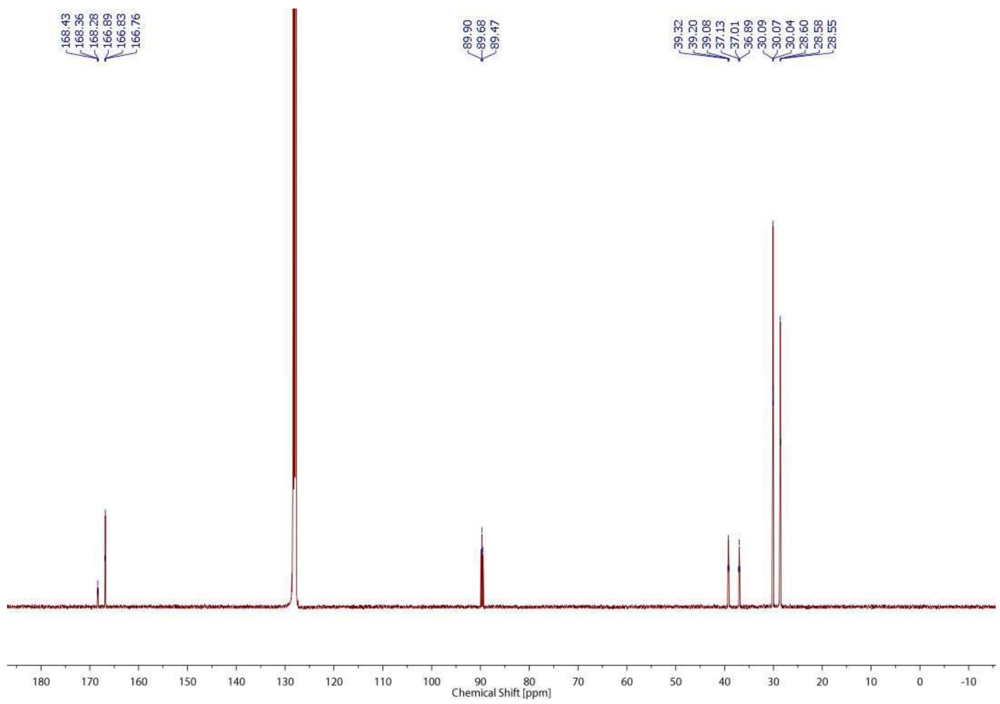



**Figure 19:** $^{13}C\{^{1}H\}$-NMR spectrum of **15**, $C_6D_6$, RT.

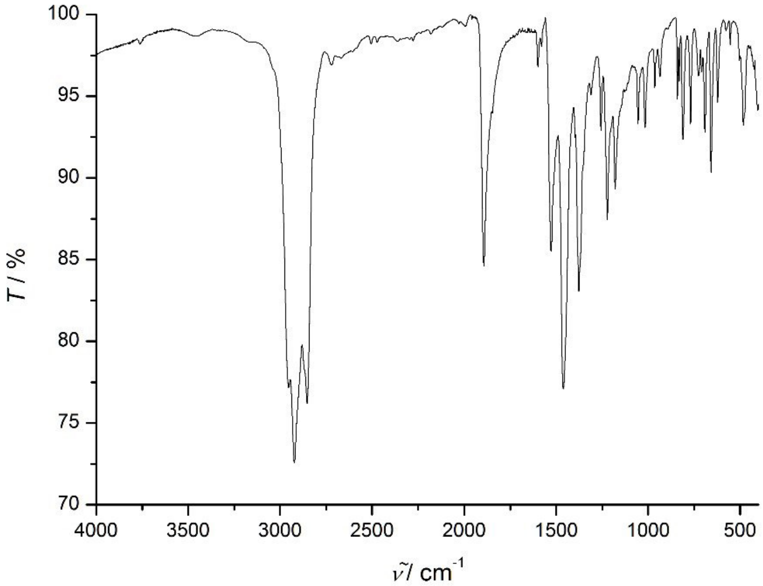



**Figure 20:** IR-Spectrum of **15**, KBr, RT.

# Crystallographic Details

CCDC-1534960 (**12**), CCDC-1534959 (**13**), CCDC-1534961 (**14**) and CCDC-1534958 (**15**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223- 336-033; e-mail: deposit@ccdc.cam.ac.uk).

**Crystallographic Details**

Suitable single crystals for X-ray structure determination were selected from the mother liquor under an inert gas atmosphere and transferred in protective perfluoro polyether oil on a microscope slide. The selected and mounted crystals were transferred to the cold gas stream on the diffractometer. The diffraction data were obtained at 100 K on a Bruker D8 three-circle diffractometer, equipped with a PHOTON 100 CMOS detector and an INCOATEC microfocus source with Quazar mirror optics (Mo-Kα radiation, λ= 0.71073 Å).

The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structures were solved and refined using the Bruker SHELX 2014 software package.[7] All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H hydrogen atoms were refined isotropically on calculated positions by using a riding model with their $U_{iso}$ values constrained to 1.5 $U_{eq}$ of their pivot atoms for terminal sp3 carbon atoms and 1.2 times for all other carbon atoms.

## X-ray Single-Crystal Structure Analysis of 12

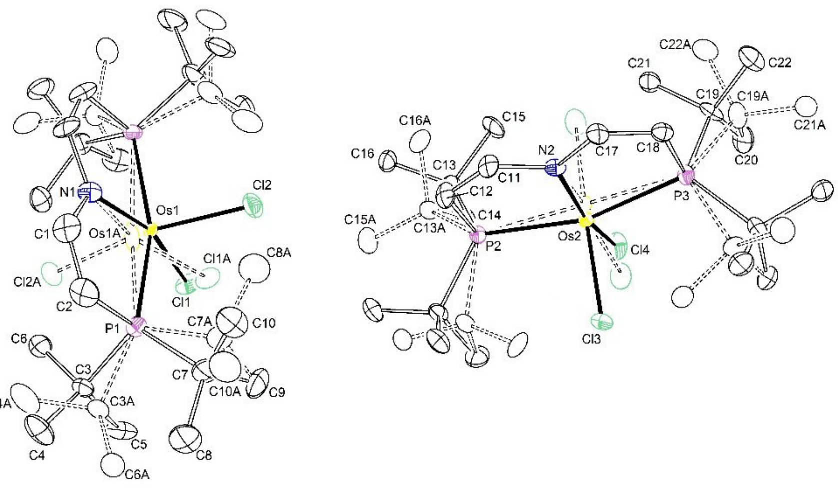



**Figure 21:** Thermal ellipsoid plot of **12** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains two half complex molecules. Both complex molecules are disordered over two positions. The first disordered complex molecule was refined with population of 0.910(3) on the main domain using some restraints (SADI) and constraints (EADP). The second disordered complex molecule was refined with population of 0.502(6) on the main domain using some restraints (SADI, RIGU) and constraints (EADP).

**Table 1:** Crystal data and structure refinement for **12**.

| | | |
|---|---|---|
| Identification code | mo_CW_JA_110116_2_0m_a (JA-i-10) | |
| Empirical formula | $C_{20}H_{40}Cl_2NOsP_2$ | |
| Formula weight | 617.57 | |
| Temperature | 102(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pnma | |
| Unit cell dimensions | a = 16.8714(6) Å | $\alpha$= 90° |
| | b = 16.9302(7) Å | $\beta$= 90° |
| | c = 17.1112(6) Å | $\gamma$ = 90° |
| Volume | 4887.6(3) Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.679 Mg/m$^3$ | |
| Absorption coefficient | 5.573 mm$^{-1}$ | |
| F(000) | 2456 | |
| Crystal size | 0.154 x 0.097 x 0.056 mm$^3$ | |
| Crystal shape and color | Block, | clear intense green |
| Theta range for data collection | 2.079 to 26.731° | |
| Index ranges | -21<=h<=21, -21<=k<=21, -21<=l<=21 | |

| | | |
|---|---|---|
| Reflections collected | 70085 | |
| Independent reflections | 5375 [R(int) = 0.0474] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Max. and min. transmission | 0.7454 and 0.5878 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5375 / 64 / 357 | |
| Goodness-of-fit on $F^2$ | 1.549 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0392, | wR2 = 0.0761 |
| R indices (all data) | R1 = 0.0459, | wR2 = 0.0784 |
| Largest diff. peak and hole | 1.331 and -2.360 $eÅ^{-3}$ | |

**Table 2:** Bond lengths [Å] and angles [°] for **12**.

| | |
|---|---|
| C(1)-C(2) | 1.323(9) |
| C(1)-N(1) | 1.409(6) |
| C(20)-C(19A) | 1.524(16) |
| C(20)-C(19) | 1.535(17) |
| C(14)-C(13A) | 1.515(12) |
| C(14)-C(13) | 1.550(12) |
| C(9)-C(7) | 1.534(8) |
| C(9)-C(7A) | 1.538(16) |
| C(13)-C(15) | 1.516(15) |
| C(13)-C(16) | 1.522(17) |
| C(13)-P(2) | 1.872(10) |
| C(19)-C(21) | 1.535(16) |
| C(19)-C(22) | 1.54(2) |
| C(19)-P(3) | 1.899(16) |
| C(13A)-C(16A) | 1.516(15) |
| C(13A)-C(15A) | 1.561(15) |
| C(13A)-P(2) | 1.915(11) |
| C(19A)-C(22A) | 1.530(16) |
| C(19A)-C(21A) | 1.547(19) |
| C(19A)-P(3) | 1.845(15) |
| C(2)-P(1) | 1.799(6) |
| C(5)-C(3) | 1.511(8) |
| C(5)-C(3A) | 1.536(15) |
| C(11)-C(12) | 1.337(10) |
| C(11)-N(2) | 1.419(9) |
| C(12)-P(2) | 1.806(8) |
| C(17)-C(18) | 1.338(10) |
| C(17)-N(2) | 1.395(9) |
| C(18)-P(3) | 1.791(8) |
| N(1)-C(1)#1 | 1.409(6) |
| N(1)-Os(1A) | 1.957(10) |
| N(1)-Os(1) | 1.966(6) |
| N(2)-Os(2) | 1.970(5) |
| P(1)-C(7) | 1.875(6) |
| P(1)-C(7A) | 1.885(19) |
| P(1)-C(3) | 1.885(6) |
| P(1)-C(3A) | 1.888(19) |
| P(1)-Os(1) | 2.3899(13) |
| P(1)-Os(1A) | 2.3924(18) |
| P(2)-C(13)#1 | 1.872(10) |
| P(2)-C(13A)#1 | 1.915(11) |
| P(2)-Os(2) | 2.3845(17) |
| P(3)-C(19A)#1 | 1.845(15) |
| P(3)-C(19)#1 | 1.899(16) |
| P(3)-Os(2) | 2.3904(18) |
| Os(2)-Cl(3) | 2.304(3) |
| Os(2)-Cl(4) | 2.382(2) |
| Cl(1)-Os(1) | 2.380(3) |
| Cl(2)-Os(1) | 2.319(2) |
| Os(1)-P(1)#1 | 2.3899(13) |
| C(3)-C(4) | 1.527(7) |
| C(3)-C(6) | 1.538(7) |
| C(7)-C(10) | 1.531(8) |
| C(7)-C(8) | 1.539(8) |
| Cl(1A)-Os(1A) | 2.40(3) |
| Cl(2A)-Os(1A) | 2.28(2) |
| Os(1A)-P(1)#1 | 2.3924(18) |
| C(3A)-C(4A) | 1.527(15) |
| C(3A)-C(6A) | 1.527(15) |
| C(7A)-C(10A) | 1.541(16) |
| C(7A)-C(8A) | 1.549(16) |
| | |
| C(2)-C(1)-N(1) | 122.1(5) |
| C(15)-C(13)-C(16) | 109.3(10) |
| C(15)-C(13)-C(14) | 110.4(8) |
| C(16)-C(13)-C(14) | 106.9(9) |
| C(15)-C(13)-P(2) | 115.6(9) |
| C(16)-C(13)-P(2) | 104.9(7) |
| C(14)-C(13)-P(2) | 109.3(6) |
| C(21)-C(19)-C(20) | 107.5(10) |
| C(21)-C(19)-C(22) | 107.9(12) |
| C(20)-C(19)-C(22) | 110.6(12) |
| C(21)-C(19)-P(3) | 114.6(10) |
| C(20)-C(19)-P(3) | 108.5(9) |
| C(22)-C(19)-P(3) | 107.7(9) |
| C(14)-C(13A)-C(16A) | 113.9(9) |
| C(14)-C(13A)-C(15A) | 107.6(9) |

| | | | |
|---|---|---|---|
| C(16A)-C(13A)-C(15A) | 107.1(10) | C(12)-P(2)-C(13A)#1 | 104.3(4) |
| C(14)-C(13A)-P(2) | 108.7(7) | C(13A)-P(2)-C(13A)#1 | 129.9(7) |
| C(16A)-C(13A)-P(2) | 113.6(8) | C(12)-P(2)-Os(2) | 98.3(2) |
| C(15A)-C(13A)-P(2) | 105.4(7) | C(18)-P(3)-C(19A)#1 | 105.0(5) |
| C(20)-C(19A)-C(22A) | 112.0(11) | C(18)-P(3)-C(19A) | 105.0(5) |
| C(20)-C(19A)-C(21A) | 106.9(10) | C(19A)#1-P(3)-C(19A) | 127.4(10) |
| C(22A)-C(19A)-C(21A) | 108.5(12) | C(18)-P(3)-C(19) | 104.8(5) |
| C(20)-C(19A)-P(3) | 111.7(9) | C(18)-P(3)-C(19)#1 | 104.8(5) |
| C(22A)-C(19A)-P(3) | 112.9(10) | C(19)-P(3)-C(19)#1 | 93.5(9) |
| C(21A)-C(19A)-P(3) | 104.4(9) | C(18)-P(3)-Os(2) | 98.4(2) |
| C(1)-C(2)-P(1) | 115.6(4) | N(2)-Os(2)-Cl(3) | 103.66(9) |
| C(12)-C(11)-N(2) | 122.5(7) | N(2)-Os(2)-Cl(4) | 160.80(9) |
| C(11)-C(12)-P(2) | 115.1(6) | Cl(3)-Os(2)-Cl(4) | 95.54(10) |
| C(18)-C(17)-N(2) | 121.2(7) | N(2)-Os(2)-P(2) | 82.94(17) |
| C(17)-C(18)-P(3) | 115.7(6) | Cl(3)-Os(2)-P(2) | 94.62(7) |
| C(1)#1-N(1)-C(1) | 116.9(6) | Cl(4)-Os(2)-P(2) | 95.75(7) |
| C(1)#1-N(1)-Os(1A) | 120.8(3) | N(2)-Os(2)-P(3) | 81.65(18) |
| C(1)-N(1)-Os(1A) | 120.8(3) | Cl(3)-Os(2)-P(3) | 96.44(7) |
| C(1)#1-N(1)-Os(1) | 121.5(3) | Cl(4)-Os(2)-P(3) | 96.27(8) |
| C(1)-N(1)-Os(1) | 121.5(3) | P(2)-Os(2)-P(3) | 162.78(6) |
| C(17)-N(2)-C(11) | 116.8(6) | N(1)-Os(1)-Cl(2) | 106.82(19) |
| C(17)-N(2)-Os(2) | 122.4(5) | N(1)-Os(1)-Cl(1) | 160.16(19) |
| C(11)-N(2)-Os(2) | 120.5(4) | Cl(2)-Os(1)-Cl(1) | 93.02(10) |
| C(2)-P(1)-C(7) | 105.4(3) | N(1)-Os(1)-P(1)#1 | 82.22(4) |
| C(2)-P(1)-C(7A) | 105.4(6) | Cl(2)-Os(1)-P(1)#1 | 96.39(4) |
| C(2)-P(1)-C(3) | 103.9(3) | Cl(1)-Os(1)-P(1)#1 | 95.85(4) |
| C(7)-P(1)-C(3) | 110.5(3) | N(1)-Os(1)-P(1) | 82.22(4) |
| C(2)-P(1)-C(3A) | 104.0(6) | Cl(2)-Os(1)-P(1) | 96.39(4) |
| C(7A)-P(1)-C(3A) | 111.0(7) | Cl(1)-Os(1)-P(1) | 95.84(4) |
| C(2)-P(1)-Os(1) | 98.2(2) | P(1)#1-Os(1)-P(1) | 162.17(7) |
| C(7)-P(1)-Os(1) | 123.55(19) | C(5)-C(3)-C(4) | 110.4(5) |
| C(3)-P(1)-Os(1) | 112.31(18) | C(5)-C(3)-C(6) | 108.0(5) |
| C(2)-P(1)-Os(1A) | 97.5(3) | C(4)-C(3)-C(6) | 108.4(5) |
| C(7A)-P(1)-Os(1A) | 112.9(9) | C(5)-C(3)-P(1) | 111.4(4) |
| C(3A)-P(1)-Os(1A) | 122.9(8) | C(4)-C(3)-P(1) | 113.4(4) |
| C(12)-P(2)-C(13)#1 | 105.3(4) | C(6)-C(3)-P(1) | 105.0(4) |
| C(12)-P(2)-C(13) | 105.3(4) | C(10)-C(7)-C(9) | 110.1(5) |
| C(13)#1-P(2)-C(13) | 86.7(8) | C(10)-C(7)-C(8) | 108.2(5) |
| C(12)-P(2)-C(13A) | 104.3(4) | C(9)-C(7)-C(8) | 109.7(6) |

| | |
|---|---|
| C(10)-C(7)-P(1) | 106.4(4) |
| C(9)-C(7)-P(1) | 108.1(4) |
| C(8)-C(7)-P(1) | 114.3(4) |
| N(1)-Os(1A)-Cl(2A) | 103.7(8) |
| N(1)-Os(1A)-P(1)#1 | 82.34(19) |
| Cl(2A)-Os(1A)-P(1)#1 | 96.9(2) |
| N(1)-Os(1A)-P(1) | 82.34(19) |
| Cl(2A)-Os(1A)-P(1) | 96.9(2) |
| P(1)#1-Os(1A)-P(1) | 161.4(4) |
| N(1)-Os(1A)-Cl(1A) | 162.5(10) |
| Cl(2A)-Os(1A)-Cl(1A) | 93.8(11) |
| P(1)#1-Os(1A)-Cl(1A) | 95.7(2) |
| P(1)-Os(1A)-Cl(1A) | 95.7(2) |
| C(4A)-C(3A)-C(6A) | 108.6(14) |
| C(4A)-C(3A)-C(5) | 109.0(14) |
| C(6A)-C(3A)-C(5) | 108.8(14) |
| C(4A)-C(3A)-P(1) | 108(3) |
| C(6A)-C(3A)-P(1) | 113(3) |
| C(5)-C(3A)-P(1) | 110.1(11) |
| C(9)-C(7A)-C(10A) | 107.9(14) |
| C(9)-C(7A)-C(8A) | 107.1(14) |
| C(10A)-C(7A)-C(8A) | 107.9(14) |
| C(9)-C(7A)-P(1) | 107.4(11) |
| C(10A)-C(7A)-P(1) | 119(3) |
| C(8A)-C(7A)-P(1) | 107(3) |

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

## X-ray Single-Crystal Structure Analysis of 13

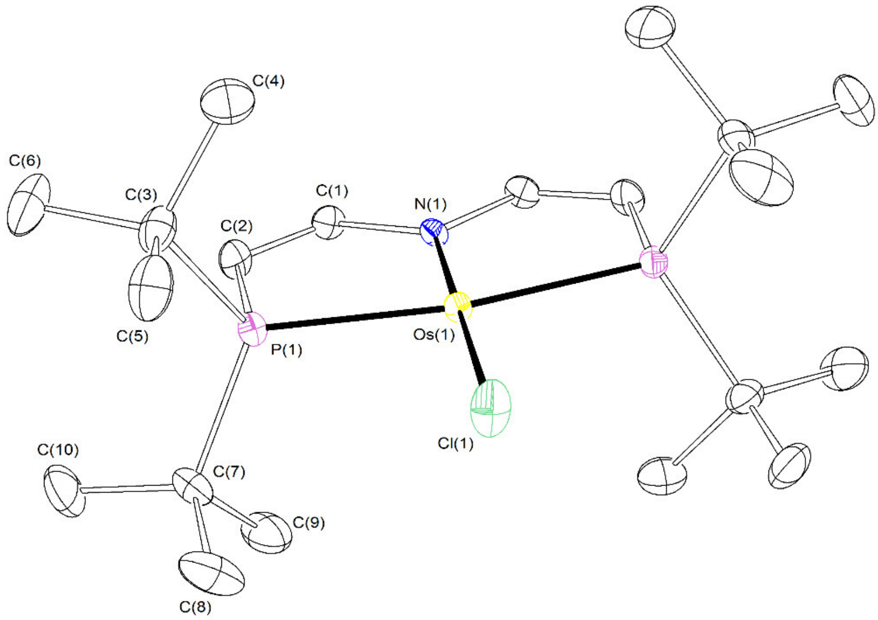



**Figure 21:** Thermal ellipsoid plot of **13** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains a half complex molecule.

**Table 3:** Crystal data and structure refinement for **13**.

| | | |
|---|---|---|
| Identification code | mo_CW_JA_020816_0m_a (JA-ii-32) | |
| Empirical formula | $C_{20}H_{40}ClNOsP_2$ | |
| Formula weight | 582.12 | |
| Temperature | 112(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2/c | |
| Unit cell dimensions | a = 11.4519(6) Å | α= 90° |
| | b = 8.5831(4) Å | β= 113.000(2)° |
| | c = 13.3683(6) Å | γ = 90° |
| Volume | 1209.55(10) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.598 Mg/m$^3$ | |
| Absorption coefficient | 5.518 mm$^{-1}$ | |
| F(000) | 580 | |
| Crystal size | 0.187 x 0.157 x 0.072 mm$^3$ | |
| Theta range for data collection | 2.373 to 28.366° | |
| Index ranges | -15<=h<=15, -10<=k<=11, -17<=l<=17 | |
| Reflections collected | 36752 | |

| | | |
|---|---|---|
| Independent reflections | 3027 [R(int) = 0.0469] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Max. and min. transmission | 0.7457 and 0.6334 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3027 / 0 / 121 | |
| Goodness-of-fit on $F^2$ | 1.122 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0161, | wR2 = 0.0301 |
| R indices (all data) | R1 = 0.0269, | wR2 = 0.0329 |
| Largest diff. peak and hole | 0.484 and -0.634 e.$Å^{-3}$ | |

**Table 4:** Bond lengths [Å] and angles [°] for **13**.

| | |
|---|---|
| C(1)-C(2) | 1.333(3) |
| C(1)-N(1) | 1.403(2) |
| C(2)-P(1) | 1.802(2) |
| C(3)-C(5) | 1.524(3) |
| C(3)-C(6) | 1.526(3) |
| C(3)-C(4) | 1.542(3) |
| C(3)-P(1) | 1.877(2) |
| C(7)-C(10) | 1.528(3) |
| C(7)-C(9) | 1.528(3) |
| C(7)-C(8) | 1.529(3) |
| C(7)-P(1) | 1.875(2) |
| N(1)-C(1)#1 | 1.403(2) |
| N(1)-Os(1) | 1.980(2) |
| P(1)-Os(1) | 2.3392(5) |
| Cl(1)-Os(1) | 2.3542(7) |
| Os(1)-P(1)#1 | 2.3392(5) |
| C(2)-C(1)-N(1) | 121.60(19) |
| C(1)-C(2)-P(1) | 115.04(16) |
| C(5)-C(3)-C(6) | 110.3(2) |
| C(5)-C(3)-C(4) | 108.57(19) |
| C(6)-C(3)-C(4) | 108.2(2) |
| C(5)-C(3)-P(1) | 110.53(16) |
| C(6)-C(3)-P(1) | 114.49(16) |
| C(4)-C(3)-P(1) | 104.33(15) |
| C(10)-C(7)-C(9) | 108.8(2) |
| C(10)-C(7)-C(8) | 109.9(2) |
| C(9)-C(7)-C(8) | 108.0(2) |
| C(10)-C(7)-P(1) | 114.67(16) |
| C(9)-C(7)-P(1) | 104.65(15) |
| C(8)-C(7)-P(1) | 110.51(15) |
| C(1)-N(1)-C(1)#1 | 117.5(2) |
| C(1)-N(1)-Os(1) | 121.25(12) |
| C(1)#1-N(1)-Os(1) | 121.25(12) |
| C(2)-P(1)-C(7) | 104.95(10) |
| C(2)-P(1)-C(3) | 104.59(10) |
| C(7)-P(1)-C(3) | 113.19(10) |
| C(2)-P(1)-Os(1) | 99.45(7) |
| C(7)-P(1)-Os(1) | 117.65(7) |
| C(3)-P(1)-Os(1) | 114.48(7) |
| N(1)-Os(1)-P(1) | 82.656(13) |
| N(1)-Os(1)-P(1)#1 | 82.656(13) |
| P(1)-Os(1)-P(1)#1 | 165.31(3) |
| N(1)-Os(1)-Cl(1) | 180.0 |
| P(1)-Os(1)-Cl(1) | 97.344(13) |
| P(1)#1-Os(1)-Cl(1) | 97.344(13) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

## X-ray Single-Crystal Structure Analysis of 14

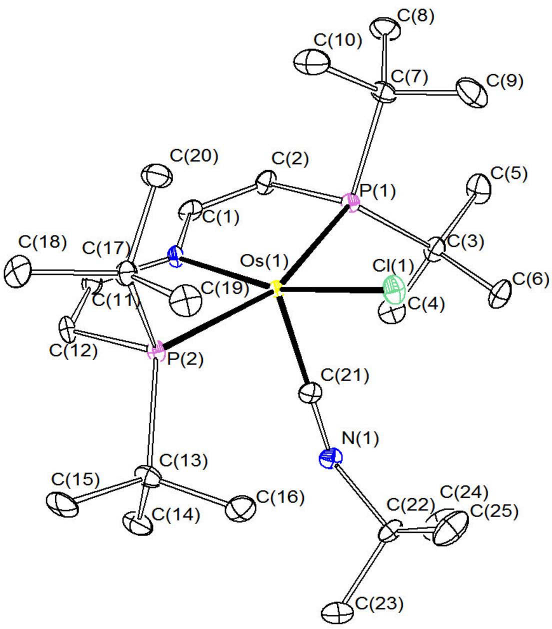



**Figure 23.** Thermal ellipsoid plot of **14** with the anisotropic displacement parameters drawn at the 50% probability level. The structure was refined using two constrains (EADP).

**Table 5:** Crystal data and structure refinement for **14**.

| | | |
|---|---|---|
| Identification code | mo_CV_JA_060516_2_0m_a | (JA-i-94) |
| Empirical formula | $C_{25}H_{49}ClN_2OsP_2$ | |
| Formula weight | 665.25 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 15.2391(7) Å | $\alpha$= 90° |
| | b = 10.9698(5) Å | $\beta$= 96.832(2)° |
| | c = 16.9742(8) Å | $\gamma$ = 90° |
| Volume | 2817.4(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.568 $Mg/m^3$ | |
| Absorption coefficient | 4.750 $mm^{-1}$ | |
| F(000) | 1344 | |
| Crystal size | 0.947 x 0.766 x 0.556 $mm^3$ | |
| Crystal shape and color | Block, | clear intense blue |
| Theta range for data collection | 2.215 to 27.197° | |
| Index ranges | -19<=h<=19, -14<=k<=14, -21<=l<=21 | |

| | | |
|---|---|---|
| Reflections collected | 76131 | |
| Independent reflections | 6264 [R(int) = 0.0694] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Max. and min. transmission | 0.7455 and 0.1448 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 6264 / 0 / 283 | |
| Goodness-of-fit on $F^2$ | 1.067 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0290, | wR2 = 0.0755 |
| R indices (all data) | R1 = 0.0349, | wR2 = 0.0797 |
| Largest diff. peak and hole | 1.645 and -2.020 eÅ$^{-3}$ | |

**Table 6:** Bond lengths [Å] and angles [°] for **14**.

| | |
|---|---|
| Os(1)-C(21) | 1.827(4) |
| Os(1)-N(2) | 2.050(3) |
| Os(1)-P(2) | 2.3688(10) |
| Os(1)-P(1) | 2.3827(10) |
| Os(1)-Cl(1) | 2.4046(9) |
| P(1)-C(2) | 1.787(4) |
| P(1)-C(3) | 1.882(4) |
| P(1)-C(7) | 1.885(4) |
| C(1)-C(2) | 1.350(6) |
| C(1)-N(2) | 1.366(5) |
| N(1)-C(21) | 1.197(5) |
| N(1)-C(22) | 1.466(5) |
| P(2)-C(12) | 1.790(4) |
| P(2)-C(13) | 1.872(4) |
| P(2)-C(17) | 1.881(4) |
| N(2)-C(11) | 1.382(5) |
| C(3)-C(5) | 1.530(6) |
| C(3)-C(6) | 1.536(6) |
| C(3)-C(4) | 1.539(6) |
| C(19)-C(17) | 1.537(6) |
| C(18)-C(17) | 1.532(5) |
| C(9)-C(7) | 1.524(6) |
| C(8)-C(7) | 1.530(6) |
| C(7)-C(10) | 1.532(6) |
| C(11)-C(12) | 1.339(6) |
| C(17)-C(20) | 1.525(6) |
| C(16)-C(13) | 1.539(6) |
| C(15)-C(13) | 1.532(6) |
| C(14)-C(13) | 1.532(6) |
| C(22)-C(24) | 1.512(6) |
| C(22)-C(23) | 1.520(6) |
| C(22)-C(25) | 1.522(6) |

| | |
|---|---|
| C(21)-Os(1)-N(2) | 101.93(15) |
| C(21)-Os(1)-P(2) | 95.07(13) |
| N(2)-Os(1)-P(2) | 81.07(9) |
| C(21)-Os(1)-P(1) | 96.11(13) |
| N(2)-Os(1)-P(1) | 81.12(9) |
| P(2)-Os(1)-P(1) | 160.58(3) |
| C(21)-Os(1)-Cl(1) | 94.20(12) |
| N(2)-Os(1)-Cl(1) | 163.87(9) |
| P(2)-Os(1)-Cl(1) | 97.55(3) |
| P(1)-Os(1)-Cl(1) | 97.40(3) |
| C(2)-P(1)-C(3) | 106.72(19) |
| C(2)-P(1)-C(7) | 103.67(19) |
| C(3)-P(1)-C(7) | 110.26(19) |
| C(2)-P(1)-Os(1) | 99.78(14) |
| C(3)-P(1)-Os(1) | 120.49(13) |
| C(7)-P(1)-Os(1) | 113.66(13) |
| C(2)-C(1)-N(2) | 123.0(4) |
| C(21)-N(1)-C(22) | 144.4(4) |
| C(12)-P(2)-C(13) | 106.64(19) |
| C(12)-P(2)-C(17) | 103.45(18) |
| C(13)-P(2)-C(17) | 110.64(19) |
| C(12)-P(2)-Os(1) | 100.30(14) |
| C(13)-P(2)-Os(1) | 123.60(14) |
| C(17)-P(2)-Os(1) | 109.77(13) |
| C(1)-N(2)-C(11) | 118.8(3) |
| C(1)-N(2)-Os(1) | 120.7(3) |
| C(11)-N(2)-Os(1) | 120.5(3) |
| C(1)-C(2)-P(1) | 115.1(3) |
| C(5)-C(3)-C(6) | 109.0(3) |
| C(5)-C(3)-C(4) | 107.6(3) |
| C(6)-C(3)-C(4) | 110.1(3) |
| C(5)-C(3)-P(1) | 115.4(3) |
| C(6)-C(3)-P(1) | 108.3(3) |
| C(4)-C(3)-P(1) | 106.5(3) |
| C(9)-C(7)-C(8) | 110.5(4) |
| C(9)-C(7)-C(10) | 108.3(4) |
| C(8)-C(7)-C(10) | 107.6(4) |
| C(9)-C(7)-P(1) | 111.5(3) |
| C(8)-C(7)-P(1) | 113.6(3) |
| C(10)-C(7)-P(1) | 105.0(3) |
| C(12)-C(11)-N(2) | 122.9(4) |
| C(20)-C(17)-C(18) | 109.2(3) |
| C(20)-C(17)-C(19) | 108.5(3) |
| C(18)-C(17)-C(19) | 110.1(4) |

| | | | |
|---|---|---|---|
| C(20)-C(17)-P(2) | 104.3(3) | N(1)-C(21)-Os(1) | 178.9(4) |
| C(18)-C(17)-P(2) | 113.5(3) | N(1)-C(22)-C(24) | 108.7(4) |
| C(19)-C(17)-P(2) | 110.9(3) | N(1)-C(22)-C(23) | 107.7(3) |
| C(14)-C(13)-C(15) | 107.4(3) | C(24)-C(22)-C(23) | 110.4(4) |
| C(14)-C(13)-C(16) | 109.6(3) | N(1)-C(22)-C(25) | 109.8(3) |
| C(15)-C(13)-C(16) | 110.2(4) | C(24)-C(22)-C(25) | 109.8(4) |
| C(14)-C(13)-P(2) | 106.4(3) | C(23)-C(22)-C(25) | 110.6(4) |
| C(15)-C(13)-P(2) | 114.2(3) | | |
| C(16)-C(13)-P(2) | 109.0(3) | | |
| C(11)-C(12)-P(2) | 114.9(3) | | |

## X-ray Single-Crystal Structure Analysis of 15

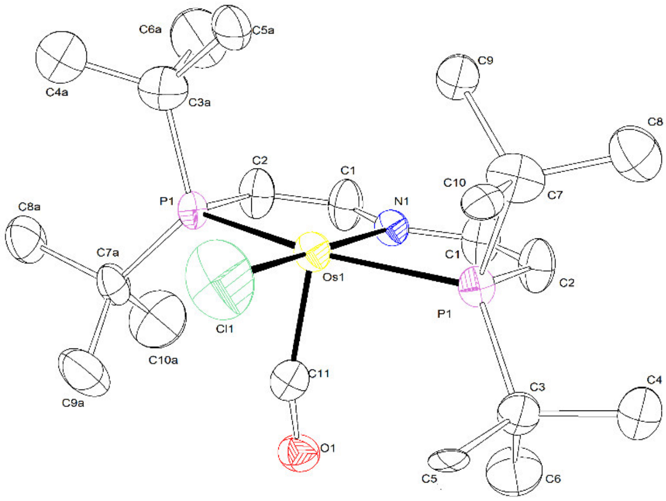



**Figure 24:** Thermal ellipsoid plot of **15** with the anisotropic displacement parameters drawn at the 50% probability level. The asymmetric unit contains a half disordered complex molecule. The disorder was refined with site occupation factors of 0.25 for both sites using PART commands and some restraints (SADI, RIGU) and constraints (EADP). The structure was refined as an inversion twin using the twin law -100 0-10 00-1 (BASF: 0.50(3)).

**Table 7:** Crystal data and structure refinement for **15**.

| | | |
|---|---|---|
| Identification code | mo_CW_JA_090117_0m_b (JA-ii-81) | |
| Empirical formula | $C_{21}H_{40}ClNOOsP_2$ | |
| Formula weight | 610.13 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Tetragonal | |
| Space group | I4 | |
| Unit cell dimensions | a = 12.0393(7) Å | $\alpha$= 90° |
| | b = 12.0393(7) Å | $\beta$= 90° |
| | c = 8.5145(5) Å | $\gamma$ = 90° |
| Volume | 1234.13(16) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.642 $Mg/m^3$ | |
| Absorption coefficient | 5.415 $mm^{-1}$ | |
| F(000) | 608 | |
| Crystal size | 0.309 x 0.180 x 0.142 $mm^3$ | |
| Crystal shape and color | Block, | dark brown |
| Theta range for data collection | 2.392 to 33.138° | |
| Index ranges | -17<=h<=18, -18<=k<=18, -13<=l<=12 | |

| | | |
|---|---|---|
| Reflections collected | 28153 | |
| Independent reflections | 2296 [R(int) = 0.0545] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Max. and min. transmission | 0.7466 and 0.5604 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2296 / 310 / 201 | |
| Goodness-of-fit on $F^2$ | 1.066 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0355, | wR2 = 0.0641 |
| R indices (all data) | R1 = 0.0520, | wR2 = 0.0685 |
| Absolute structure parameter | 0.50(3) | |
| Largest diff. peak and hole | 1.354 and -1.026 eÅ$^{-3}$ | |

**Table 8:** Bond lengths [Å] and angles [°] for **15**.

| | |
|---|---|
| Os(1)-C(11)#1 | 1.85(3) |
| Os(1)-C(11)#2 | 1.85(3) |
| Os(1)-C(11) | 1.85(3) |
| Os(1)-C(11)#3 | 1.85(3) |
| Os(1)-N(1) | 2.19(2) |
| Os(1)-Cl(1) | 2.240(9) |
| Os(1)-P(1) | 2.394(4) |
| Os(1)-P(1)#2 | 2.394(4) |
| Os(1)-P(1)#3 | 2.394(4) |
| Os(1)-P(1)#1 | 2.394(4) |
| N(1)-C(1)#1 | 1.322(17) |
| N(1)-C(1) | 1.322(17) |
| N(1)-C(1)#2 | 1.322(17) |
| N(1)-C(1)#3 | 1.322(17) |
| P(1)-O(1) | 0.704(19) |
| P(1)-C(2) | 1.744(15) |
| P(1)-C(7A) | 1.80(2) |
| P(1)-C(3A) | 1.83(5) |
| P(1)-C(3) | 1.85(2) |
| P(1)-C(7) | 1.87(3) |
| C(1)-C(2) | 1.379(19) |
| C(3A)-C(4A) | 1.52(4) |
| C(3A)-C(6A) | 1.54(4) |
| C(3A)-C(5A) | 1.54(3) |
| C(5A)-O(1)#2 | 1.89(4) |
| C(7A)-O(1) | 1.43(3) |
| C(7A)-C(9A) | 1.56(2) |
| C(7A)-C(8A) | 1.56(2) |
| C(7A)-C(10A) | 1.59(2) |
| C(5)-C(3) | 1.51(4) |
| C(3)-C(9)#2 | 0.88(4) |
| C(3)-O(1) | 1.49(3) |
| C(3)-C(6) | 1.50(4) |
| C(3)-C(4) | 1.59(3) |
| C(7)-C(8) | 1.55(2) |
| C(7)-C(10) | 1.56(2) |
| C(7)-C(9) | 1.57(2) |
| C(7)-O(1) | 1.71(3) |
| C(7)-C(6)#3 | 1.73(5) |
| C(7)-C(11) | 2.04(4) |
| C(8)-C(6)#3 | 1.96(5) |
| C(6)-C(8)#2 | 1.96(5) |
| C(11)-O(1) | 1.27(3) |
| O(1)-C(9)#2 | 1.87(3) |
| O(1)-C(5A)#3 | 1.89(4) |
| | |
| C(11)#1-Os(1)-C(11)#2 | 89.3(2) |
| C(11)#1-Os(1)-C(11) | 167.3(18) |
| C(11)#2-Os(1)-C(11) | 89.3(2) |
| C(11)#1-Os(1)-C(11)#3 | 89.3(2) |
| C(11)#2-Os(1)-C(11)#3 | 167.3(18) |
| C(11)-Os(1)-C(11)#3 | 89.3(2) |
| C(11)#1-Os(1)-N(1) | 96.4(9) |
| C(11)#2-Os(1)-N(1) | 96.4(9) |
| C(11)-Os(1)-N(1) | 96.4(9) |
| C(11)#3-Os(1)-N(1) | 96.4(9) |
| C(11)#1-Os(1)-Cl(1) | 83.6(9) |
| C(11)#2-Os(1)-Cl(1) | 83.6(9) |
| C(11)-Os(1)-Cl(1) | 83.6(9) |
| C(11)#3-Os(1)-Cl(1) | 83.6(9) |
| N(1)-Os(1)-Cl(1) | 180.0 |
| C(11)#1-Os(1)-P(1) | 176.2(9) |
| C(11)#2-Os(1)-P(1) | 91.4(9) |
| C(11)-Os(1)-P(1) | 16.5(9) |
| C(11)#3-Os(1)-P(1) | 90.8(8) |
| N(1)-Os(1)-P(1) | 79.81(8) |
| Cl(1)-Os(1)-P(1) | 100.19(8) |
| C(11)#1-Os(1)-P(1)#2 | 91.4(9) |
| C(11)#2-Os(1)-P(1)#2 | 16.5(9) |
| C(11)-Os(1)-P(1)#2 | 90.8(8) |
| C(11)#3-Os(1)-P(1)#2 | 176.2(9) |
| N(1)-Os(1)-P(1)#2 | 79.81(8) |
| Cl(1)-Os(1)-P(1)#2 | 100.19(8) |
| P(1)-Os(1)-P(1)#2 | 88.21(3) |
| C(11)#1-Os(1)-P(1)#3 | 90.8(8) |
| C(11)#2-Os(1)-P(1)#3 | 176.2(9) |
| C(11)-Os(1)-P(1)#3 | 91.4(9) |

| | | | |
|---|---|---|---|
| C(11)#3-Os(1)-P(1)#3 | 16.5(9) | C(3)-P(1)-Os(1) | 123.1(8) |
| N(1)-Os(1)-P(1)#3 | 79.81(8) | C(7)-P(1)-Os(1) | 105.3(8) |
| Cl(1)-Os(1)-P(1)#3 | 100.19(8) | N(1)-C(1)-C(2) | 125.7(15) |
| P(1)-Os(1)-P(1)#3 | 88.21(3) | C(1)-C(2)-P(1) | 115.5(10) |
| P(1)#2-Os(1)-P(1)#3 | 159.63(16) | C(4A)-C(3A)-C(6A) | 106(4) |
| C(11)#1-Os(1)-P(1)#1 | 16.5(9) | C(4A)-C(3A)-C(5A) | 113(4) |
| C(11)#2-Os(1)-P(1)#1 | 90.8(8) | C(6A)-C(3A)-C(5A) | 88(4) |
| C(11)-Os(1)-P(1)#1 | 176.2(9) | C(4A)-C(3A)-P(1) | 120(2) |
| C(11)#3-Os(1)-P(1)#1 | 91.4(9) | C(6A)-C(3A)-P(1) | 112(2) |
| N(1)-Os(1)-P(1)#1 | 79.81(8) | C(5A)-C(3A)-P(1) | 113(2) |
| Cl(1)-Os(1)-P(1)#1 | 100.19(8) | C(3A)-C(5A)-O(1)#2 | 144(3) |
| P(1)-Os(1)-P(1)#1 | 159.63(16) | O(1)-C(7A)-C(9A) | 123.3(18) |
| P(1)#2-Os(1)-P(1)#1 | 88.21(3) | O(1)-C(7A)-C(8A) | 93.8(15) |
| P(1)#3-Os(1)-P(1)#1 | 88.21(3) | C(9A)-C(7A)-C(8A) | 106.3(17) |
| C(1)#1-N(1)-C(1) | 126(2) | O(1)-C(7A)-C(10A) | 120.3(19) |
| C(1)#1-N(1)-C(1)#2 | 77.9(9) | C(9A)-C(7A)-C(10A) | 105.0(16) |
| C(1)-N(1)-C(1)#2 | 77.9(9) | C(8A)-C(7A)-C(10A) | 104.9(16) |
| C(1)#1-N(1)-C(1)#3 | 77.9(9) | O(1)-C(7A)-P(1) | 21.5(8) |
| C(1)-N(1)-C(1)#3 | 77.9(9) | C(9A)-C(7A)-P(1) | 114.8(15) |
| C(1)#2-N(1)-C(1)#3 | 126(2) | C(8A)-C(7A)-P(1) | 115.2(13) |
| C(1)#1-N(1)-Os(1) | 117.2(10) | C(10A)-C(7A)-P(1) | 109.6(16) |
| C(1)-N(1)-Os(1) | 117.2(10) | C(9)#2-C(3)-O(1) | 101(3) |
| C(1)#2-N(1)-Os(1) | 117.2(10) | C(9)#2-C(3)-C(6) | 40(3) |
| C(1)#3-N(1)-Os(1) | 117.2(10) | O(1)-C(3)-C(6) | 120(3) |
| O(1)-P(1)-C(2) | 104.9(17) | C(9)#2-C(3)-C(5) | 93(4) |
| O(1)-P(1)-C(7A) | 48.4(16) | O(1)-C(3)-C(5) | 113(2) |
| C(2)-P(1)-C(7A) | 96.0(9) | C(6)-C(3)-C(5) | 112(2) |
| O(1)-P(1)-C(3A) | 70.6(17) | C(9)#2-C(3)-C(4) | 144(4) |
| C(2)-P(1)-C(3A) | 93.2(12) | O(1)-C(3)-C(4) | 92.0(19) |
| C(7A)-P(1)-C(3A) | 118.6(10) | C(6)-C(3)-C(4) | 105(3) |
| O(1)-P(1)-C(3) | 49.3(17) | C(5)-C(3)-C(4) | 113(2) |
| C(2)-P(1)-C(3) | 106.8(13) | C(9)#2-C(3)-P(1) | 80(3) |
| O(1)-P(1)-C(7) | 66.2(16) | O(1)-C(3)-P(1) | 21.0(8) |
| C(2)-P(1)-C(7) | 105.3(10) | C(6)-C(3)-P(1) | 104(2) |
| C(3)-P(1)-C(7) | 112.8(11) | C(5)-C(3)-P(1) | 111.7(18) |
| O(1)-P(1)-Os(1) | 153.4(17) | C(4)-C(3)-P(1) | 110.7(18) |
| C(2)-P(1)-Os(1) | 101.7(5) | C(8)-C(7)-C(10) | 107.7(17) |
| C(7A)-P(1)-Os(1) | 127.2(6) | C(8)-C(7)-C(9) | 107.7(17) |
| C(3A)-P(1)-Os(1) | 109.6(9) | C(10)-C(7)-C(9) | 106.3(18) |

| | |
|---|---|
| C(8)-C(7)-O(1) | 101(2) |
| C(10)-C(7)-O(1) | 98.8(17) |
| C(9)-C(7)-O(1) | 134(2) |
| C(8)-C(7)-C(6)#3 | 73.3(19) |
| C(10)-C(7)-C(6)#3 | 122(2) |
| C(9)-C(7)-C(6)#3 | 34.8(18) |
| O(1)-C(7)-C(6)#3 | 138(2) |
| C(8)-C(7)-P(1) | 115(2) |
| C(10)-C(7)-P(1) | 108.6(16) |
| C(9)-C(7)-P(1) | 111.6(19) |
| O(1)-C(7)-P(1) | 22.1(7) |
| C(6)#3-C(7)-P(1) | 123(2) |
| C(8)-C(7)-C(11) | 138(2) |
| C(10)-C(7)-C(11) | 92.4(16) |
| C(9)-C(7)-C(11) | 101.4(18) |
| O(1)-C(7)-C(11) | 38.3(11) |
| C(6)#3-C(7)-C(11) | 126(2) |
| P(1)-C(7)-C(11) | 23.6(9) |
| C(7)-C(8)-C(6)#3 | 57.5(17) |
| C(3)-C(6)-C(8)#2 | 139(3) |
| O(1)-C(11)-Os(1) | 154(2) |
| O(1)-C(11)-C(7) | 56.6(15) |
| Os(1)-C(11)-C(7) | 122.0(15) |
| P(1)-O(1)-C(11) | 36.2(16) |
| P(1)-O(1)-C(7A) | 110(2) |
| C(11)-O(1)-C(7A) | 109(2) |
| P(1)-O(1)-C(3) | 110(2) |
| C(11)-O(1)-C(3) | 101(2) |
| P(1)-O(1)-C(7) | 91.7(18) |
| C(11)-O(1)-C(7) | 85.0(18) |
| C(3)-O(1)-C(7) | 151(2) |
| P(1)-O(1)-C(9)#2 | 82.2(18) |
| C(11)-O(1)-C(9)#2 | 80.4(18) |
| C(3)-O(1)-C(9)#2 | 27.8(15) |
| C(7)-O(1)-C(9)#2 | 163(2) |
| P(1)-O(1)-C(5A)#3 | 83.8(18) |
| C(11)-O(1)-C(5A)#3 | 84.4(19) |
| C(7A)-O(1)-C(5A)#3 | 27.0(12) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z #2 y,-x+1,z #3 -y+1,x,z

## Computational Details

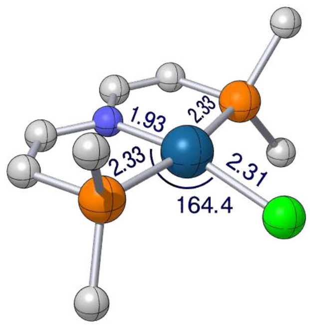
The molecular geometries of two singlet and two triplet isomers of **13** in $C_2$ and $C_\mathrm{s}$ symmetry were optimized under gas-phase conditions using the Gaussian09 program[8] with the PBE0 hybrid functional[9,10] in conjunction with Grimme's 3rd generation atom-pairwise dispersion correction including Becke–Johnson damping (D3BJ).[11] The def2-TZVP orbital basis set[12] was employed with the quasi-relativistic ECP60MWB pseudopotential,[13] which replaces the 60 core electrons in osmium. This level of DFT is abbreviated as PBE0D/TZVP. The optimized geometries were identified as minima through analysis of the eigenvalues of the Hessian matrix. Further calculations were conducted on a smaller model system, in which the four *t*Bu groups of the pincer were replaced by methyl groups (**13,Me**). For each fully optimized electronic state of the real system **13**, the model systems **13,Me** were constructed in constrained geometries where only the C–H bond lenghts of the twelve newly added hydrogen atoms (which replace the twelve methyl fragments of the four *t*Bu groups) were allowed to relax, i.e., all angles and dihedrals are kept fixed and all remaining coordinates are unaltered.

Relative energies from correlated wavefunction theory were computed at the DFT molecular geometries for the electromers of the **13,Me** model system using the Molpro2015.1 program.[14] The explicitly correlated coupled-cluster ansatz with single and double excitations and perturbative triples, CCSD(T)-F12b,[15,16] was employed in combination with the F12-optimized correlation-consistent polarized double- and triple-zeta orbital and auxiliary basis sets of the cc-pV$n$Z-F12 family[17–19] on non-metal atoms and the aug-cc-pV$n$Z-PP orbital basis set which includes the relativistic ECP60MDF pseudopotential on Os[20] in conjunction with the auxiliary def2-QZVPP/JKfit basis sets[21] for the many-electron integrals (CABS) as well as for the density-fitting of the Fock and exchange matrices (JKfit) and with the aug-cc-pV$n$Z/MP2fit basis set[22] for the remaining integrals. The CCSD(T)-F12 energies were extrapolated to the complete basis set limit CBS(D,T) according to the procedure of Hill *et al.*[23] Final energies given in the text are based on an ONIOM(CCSD(T)-F12 : PBE0D) approach according to $E_\mathrm{tot}(\mathbf{13}) = E_\mathrm{CCSD(T)\text{-}F12}(\mathbf{13,Me}) - E_\mathrm{PBE0D}(\mathbf{13,Me}) + E_\mathrm{PBE0D}(\mathbf{13})$.

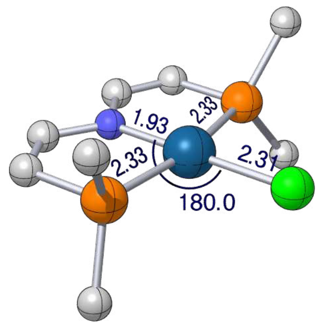
Quasi-degenerate perturbation theory (QDPT) was used to calculate spin-orbit eigenstates for the real system **13**. Computations were performed on the DFT-optimized geometry of the lowest-energy $C_2$-symmetric $^3$B state based on a CASSCF wavefunction within the ORCA program.[24,25] The ZORA approximation[26] was employed along with the ZORA-def2TZVP basis sets[27] for all elements. The active space comprises the five Os-based 5d orbitals and five occupied ligand–metal based orbitals, giving rise to a CAS(16,10) expansion. In the CASSCF calculations the orbitals were optimized by the average of 5 quintet, 45 triplet and 50 singlet roots arising from the formal d$^6$ configuration of the osmium(II) center. The RI and RIJCOSX[28] approximations were used along with the corresponding def2TZVP/C auxiliary basis sets[29] and a fine grid (GridX6 in ORCA convention), respectively. The final energies are obtained from NEVPT2 calculations,[30–32] and the energies that enter QDPT treatment via a full SOMF operator[33] are thus corrected to second order (dynamic correlation).

## Geometries and Electronic Structures

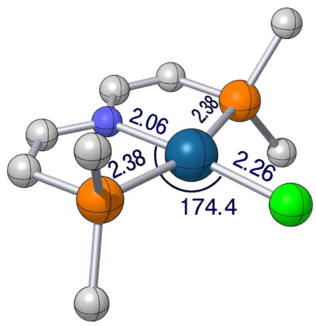
Two singlet and two triplet isomers of **13** in $C_2$ and $C_s$ symmetry were considered in the calculations, all of which correspond to local minima on the potential energy surface.



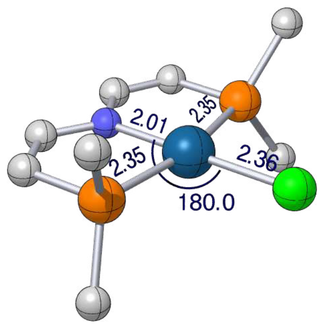

$^1$A′ ($C_s$)




$^1$A ($C_2$)




$^3$A″ ($C_s$)




$^3$B ($C_2$)

**Figure 25:** Molecular geometries for singlet and triplet isomers of **13** computed using PBE0D/TZVP; *t*Bu groups and hydrogen atoms omitted for clarity.

## Molecular Orbital Diagrams

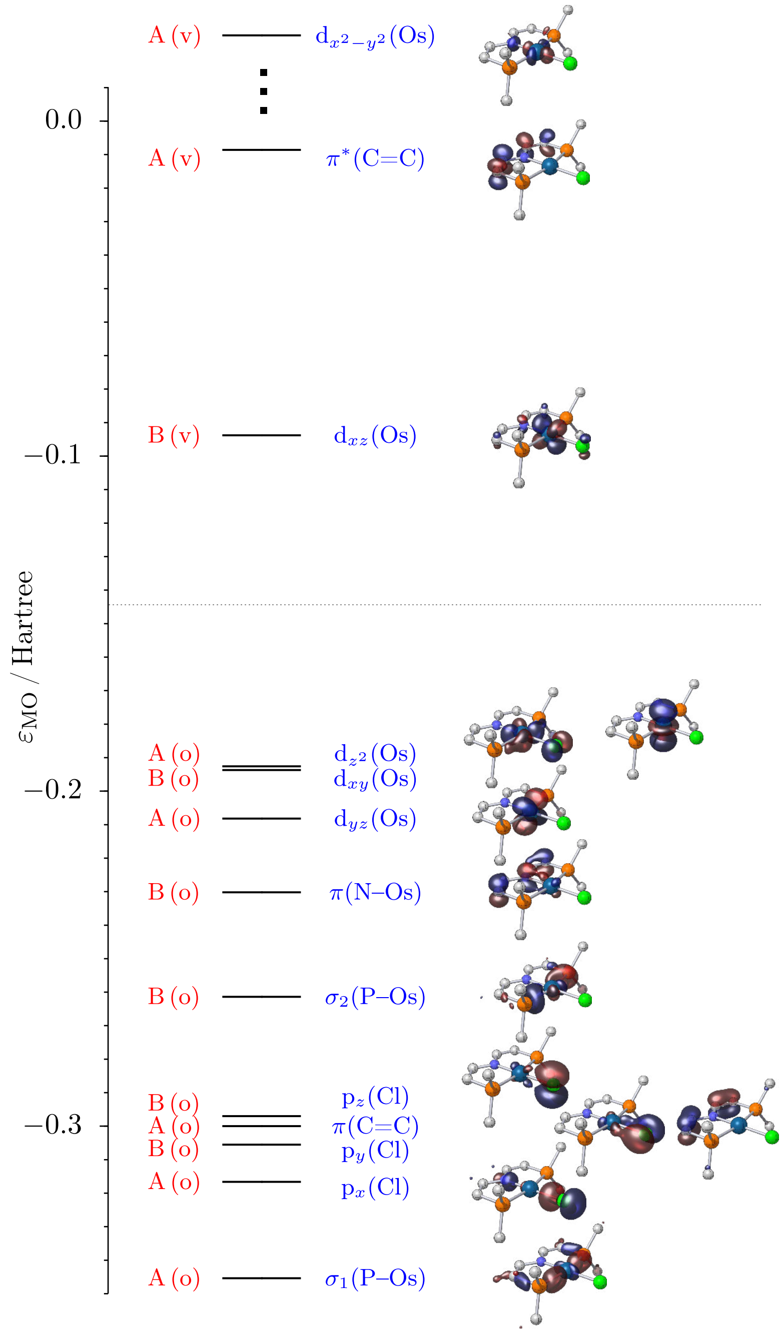



**Figure 26:** MO scheme for the $C_2$-symmetric singlet isomer of **13,Me** computed using PBE0D/TZVP; symmetry labels and orbital plots at an isovalue of 0.075 $a_0^{-3/2}$ are also given.

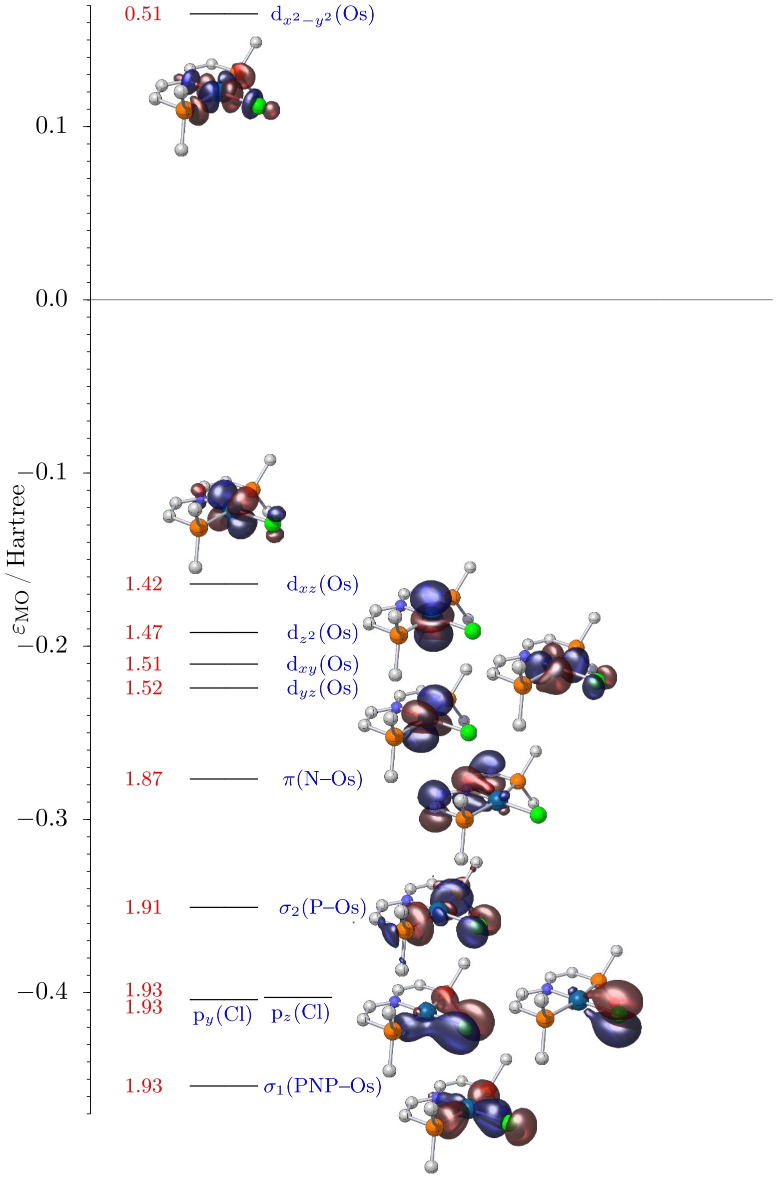



**Figure 27:** Active MO scheme computed at the $C_2$-symmetric triplet geometry of **13** for a SA-CASSCF(16,10) wavefunction, state-averaged over the 5 quintet, 45 triplet, and 50 singlet CSFs, which arise from the local $5d^6$ configuration of the formal $Os^{II}$ center; average occupation numbers (red) and orbital labels (blue) with orbital plots at an isovalue of 0.05 $a_0^{-3/2}$ are also given.

## Energies

**Table 9:** Total energies $E_{tot}$ in Hartree and relative energies $E_{rel}$ in kcal mol$^{-1}$ for the Me-truncated model system **13,Me** and the full complex **13**, computed at the PBE0D/TZVP, CCSD(T)-F12/CBS(D,T) and ONIOM levels.[a]

| | PBE0D/TZVP | | CCSD(T)-F12b | | | ONIOM[a] |
|---|---|---|---|---|---|---|
| | | | VDZ-F12 | VTZ-F12 | CBS(D,T) | |
| | **13** | **13,Me** | **13,Me** | **13,Me** | **13,Me** | **13** |
| | | | $E_{tot}$/Hartree | | | |
| $^1$A′ ($C_s$) | −2073.651 174 | −1602.270 778 | −1600.771 485 | −1600.872 070 | −1600.904 387 | −2072.284 783 |
| $^1$A ($C_2$) | −2073.649 772 | −1602.270 129 | −1600.771 452 | −1600.872 069 | −1600.904 406 | −2072.284 049 |
| $^3$A″ ($C_s$) | −2073.649 959 | −1602.268 788 | −1600.760 068 | −1600.860 296 | −1600.892 408 | −2072.273 580 |
| $^3$B ($C_2$) | −2073.667 070 | −1602.283 186 | −1600.771 010 | −1600.871 094 | −1600.903 223 | −2072.287 107 |
| | | | $E_{rel}$/kcal mol$^{-1}$ | | | |
| $^1$A′ ($C_s$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $^1$A ($C_2$) | 0.9 | 0.4 | 0.0 | 0.0 | 0.0 | 0.3 |
| $^3$A″ ($C_s$) | 0.8 | 1.2 | 7.2 | 7.4 | 0.5 | 7.0 |
| $^3$B ($C_2$) | −10.0 | −7.8 | 0.3 | 0.6 | 0.7 | −1.5 |

[a] ONIOM(CCSD(T)-F12/CBS(D,T) : PBE0D/TZVP) energy according to

$$E_{tot}^{\mathbf{13}}(\text{ONIOM}) = E_{tot}^{\mathbf{13,Me}}(\text{CCSD(T)-F12/CBS(D,T)}) - E_{tot}^{\mathbf{13,Me}}(\text{PBE0D/TZVP}) + E_{tot}^{\mathbf{13}}(\text{PBE0D/TZVP})$$

**Table 10:** State energies sorted by spin multiplicity $\Delta E_{\text{state}}$ and spin-orbit eigenvalues $\Delta E_{\text{SOC}}$ in $cm^{-1}$ from NEVPT2/SA-CASSCF(16,10)/def2TZVP(ZORA) calculations for **13**.

| | | $\Delta E_{\text{state}}$ | | | | $\Delta E_{\text{state}}$ | | $\Delta E_{\text{SOC}}$ | |
|---|---|---|---|---|---|---|---|---|---|
| root | mult | CAS(16,10) | NEVPT2 | root | mult | CAS(16,10) | NEVPT2 | CAS(16,10) | NEVPT2 |
| 0 | 1 | 5713.6 | 2159.1 | 0 | 3 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1 | 1 | 8420.0 | 7528.0 | 1 | 3 | 4414.9 | 4287.5 | 670.5 | 987.6 |
| 2 | 1 | 8974.0 | 8096.0 | 2 | 3 | 4803.7 | 4760.9 | 1535.6 | 1694.5 |
| 3 | 1 | 13 532.3 | 10 097.8 | 3 | 3 | 6181.2 | 7422.2 | 2684.8 | 2146.5 |
| 4 | 1 | 15 134.6 | 15 265.4 | 4 | 3 | 10 938.3 | 10 422.1 | 3221.6 | 3487.8 |
| 5 | 1 | 15 430.5 | 13 163.3 | 5 | 3 | 15 432.0 | 14 329.3 | 6954.9 | 7059.4 |
| 6 | 1 | 18 130.0 | 18 105.2 | 6 | 3 | 37 407.7 | 13 057.7 | 7401.3 | 7079.2 |
| 7 | 1 | 22 541.0 | 20 343.1 | 7 | 3 | 38 640.9 | 14 806.1 | 7450.0 | 7635.6 |
| 8 | 1 | 23 621.9 | 21 295.1 | 8 | 3 | 39 958.4 | 38 473.2 | 7539.2 | 7926.0 |
| 9 | 1 | 32 077.1 | 26 741.4 | 9 | 3 | 40 390.1 | 28 549.8 | 8289.3 | 8795.8 |
| 10 | 1 | 39 267.3 | 15 575.0 | 10 | 3 | 40 660.5 | 37 512.7 | 9150.9 | 8995.2 |
| 11 | 1 | 40 653.5 | 17 820.5 | 11 | 3 | 41 150.1 | 33 332.6 | 9901.4 | 9220.7 |
| 12 | 1 | 41 125.6 | 22 251.7 | 12 | 3 | 42 200.4 | 38 589.0 | 10 018.8 | 10 270.0 |
| 13 | 1 | 43 565.5 | 24 902.2 | 13 | 3 | 42 838.1 | 24 999.4 | 11 014.2 | 11 344.2 |
| 14 | 1 | 44 820.3 | 40 883.7 | 14 | 3 | 43 647.8 | 40 706.1 | 12 361.0 | 11 927.4 |
| 15 | 1 | 45 945.0 | 22 216.9 | 15 | 3 | 44 590.5 | 43 551.7 | 12 377.6 | 12 364.9 |
| 16 | 1 | 46 223.4 | 42 551.8 | 16 | 3 | 44 782.5 | 42 812.5 | 13 926.8 | 13 139.9 |
| 17 | 1 | 47 498.5 | 42 804.0 | 17 | 3 | 45 103.4 | 22 398.6 | 14 847.6 | 13 618.5 |
| 18 | 1 | 48 186.2 | 44 998.7 | 18 | 3 | 46 543.9 | 45 429.0 | 15 540.9 | 14 315.1 |
| 19 | 1 | 50 214.4 | 42 111.8 | 19 | 3 | 46 847.7 | 46 751.0 | 18 050.2 | 14 633.7 |
| 20 | 1 | 50 902.6 | 28 526.6 | 20 | 3 | 48 200.8 | 46 071.1 | 18 069.5 | 14 642.9 |
| 21 | 1 | 51 437.8 | 49 101.5 | 21 | 3 | 48 778.0 | 44 808.9 | 19 114.2 | 14 834.8 |
| 22 | 1 | 52 420.0 | 49 583.8 | 22 | 3 | 50 034.3 | 49 383.1 | 19 343.5 | 16 064.7 |
| 23 | 1 | 53 339.1 | 38 603.7 | 23 | 3 | 50 159.4 | 22 082.6 | 19 725.3 | 16 475.8 |
| 24 | 1 | 54 251.8 | 52 703.2 | 24 | 3 | 50 365.8 | 49 722.9 | 21 509.2 | 17 527.8 |
| 25 | 1 | 54 491.6 | 38 404.0 | 25 | 3 | 50 770.0 | 47 425.8 | 25 717.1 | 18 132.7 |
| 26 | 1 | 54 649.7 | 51 041.9 | 26 | 3 | 51 516.2 | 49 987.9 | 26 980.4 | 18 330.3 |
| 27 | 1 | 54 705.4 | 37 736.0 | 27 | 3 | 51 644.2 | 44 237.4 | 32 314.5 | 18 388.4 |
| 28 | 1 | 54 959.2 | 37 491.7 | 28 | 3 | 51 842.3 | 36 649.1 | 32 356.2 | 18 839.3 |
| 29 | 1 | 56 055.8 | 43 215.2 | 29 | 3 | 52 328.6 | 50 670.6 | 32 412.4 | 19 003.4 |
| 30 | 1 | 56 368.7 | 53 866.5 | 30 | 3 | 52 415.5 | 39 281.5 | 32 595.4 | 19 382.3 |
| 31 | 1 | 56 926.4 | 47 587.1 | 31 | 3 | 52 978.3 | 37 861.4 | 32 692.6 | 20 670.1 |
| 32 | 1 | 57 088.6 | 51 631.3 | 32 | 3 | 54 234.9 | 50 758.5 | 35 613.1 | 21 630.3 |
| 33 | 1 | 57 313.9 | 52 697.0 | 33 | 3 | 54 547.6 | 33 310.9 | 35 857.2 | 23 882.6 |
| 34 | 1 | 59 092.9 | 42 512.9 | 34 | 3 | 54 569.8 | 38 147.9 | 36 309.2 | 24 035.8 |
| 35 | 1 | 59 579.8 | 45 379.6 | 35 | 3 | 54 668.0 | 36 835.3 | 36 615.6 | 24 915.3 |
| 36 | 1 | 59 946.8 | 48 430.8 | 36 | 3 | 56 645.5 | 47 844.6 | 37 560.1 | 24 971.5 |
| 37 | 1 | 60 081.4 | 53 926.5 | 37 | 3 | 57 152.0 | 50 578.9 | 37 608.7 | 25 005.1 |
| 38 | 1 | 60 995.3 | 41 310.6 | 38 | 3 | 57 277.3 | 43 605.6 | 38 366.1 | 25 588.5 |
| 39 | 1 | 61 592.8 | 56 877.8 | 39 | 3 | 58 775.9 | 42 925.7 | 38 435.3 | 26 395.7 |
| 40 | 1 | 62 765.5 | 44 295.1 | 40 | 3 | 58 914.1 | 56 050.8 | 38 442.8 | 26 605.5 |
| 41 | 1 | 64 900.9 | 60 167.5 | 41 | 3 | 61 357.0 | 44 053.6 | 38 553.8 | 27 037.5 |
| 42 | 1 | 66 784.5 | 49 117.9 | 42 | 3 | 63 492.3 | 55 309.0 | 38 967.5 | 27 058.8 |
| 43 | 1 | 68 362.9 | 56 102.3 | 43 | 3 | 64 526.3 | 47 688.3 | 39 268.5 | 27 207.5 |
| 44 | 1 | 68 823.8 | 54 731.9 | 44 | 3 | 64 805.5 | 51 796.5 | 39 770.0 | 27 324.3 |
| 45 | 1 | 69 561.4 | 61 968.4 | 0 | 5 | 30 825.9 | 32 049.4 | 39 983.8 | 27 490.9 |
| 46 | 1 | 71 292.6 | 52 989.8 | 1 | 5 | 34 579.0 | 35 719.9 | 39 990.0 | 28 799.7 |
| 47 | 1 | 72 353.0 | 53 346.5 | 2 | 5 | 37 561.7 | 37 971.4 | 41 381.8 | 30 908.2 |
| 48 | 1 | 72 899.0 | 53 014.6 | 3 | 5 | 41 004.9 | 43 471.4 | ... | ... |
| 49 | 1 | 73 372.4 | 57 462.0 | 4 | 5 | 61 169.6 | 42 738.1 | ... | ... |

## Cartesian coordinates of PBE0D/TZVP geometries (Å) for 13 and 13,Me

65

13 $^1$A′ (C$_s$): $E_{tot}$(PBE0D/TZVP) = -2073.65117433

| | | | |
|---|---|---|---|
| Os | 0.010583500130 | -0.039205429854 | 0.000000000000 |
| N | 0.379781873368 | 1.858996767759 | 0.000000000000 |
| P | 0.062082579459 | 0.233199327036 | 2.314665703588 |
| P | 0.062082579459 | 0.233199327036 | -2.314665703588 |
| C | 0.359180671626 | 2.014423381165 | 2.385752352981 |
| H | 0.449490784467 | 2.600501817203 | 3.290957045670 |
| C | 0.359180671626 | 2.014423381165 | -2.385752352981 |
| H | 0.449490784467 | 2.600501817203 | -3.290957045670 |
| C | 0.481619114072 | 2.593802130300 | 1.189504560211 |
| H | 0.672794479736 | 3.659706952431 | 1.079416470417 |
| C | 0.481619114072 | 2.593802130300 | -1.189504560211 |
| H | 0.672794479736 | 3.659706952431 | -1.079416470417 |
| Cl | -1.023924465457 | -2.104222874565 | 0.000000000000 |
| C | -1.521349040810 | 0.015562612143 | 3.298778366664 |
| C | 1.542539505810 | -0.524009445309 | -3.185798142593 |
| C | 1.542539505810 | -0.524009445309 | 3.185798142593 |
| C | -1.521349040810 | 0.015562612143 | -3.298778366664 |
| C | -1.741964334889 | -1.458437626948 | 3.624167384480 |
| H | -1.645924195281 | -2.082898676248 | 2.733651267324 |
| H | -2.754944514437 | -1.586491213443 | 4.019586350416 |
| H | -1.047131828462 | -1.818245872677 | 4.384993488556 |
| C | -2.637361055400 | 0.489798157877 | 2.365783927190 |
| H | -2.699442689976 | -0.131959548163 | 1.472457976124 |
| H | -2.481846868869 | 1.524038242118 | 2.049051631298 |
| H | -3.592258008500 | 0.436969803308 | 2.899520480323 |
| C | -1.573832885873 | 0.853674312961 | 4.572376805859 |
| H | -1.505383508415 | 1.920610003378 | 4.352185939179 |
| H | -0.791015280184 | 0.597621424849 | 5.284739913292 |
| H | -2.536830603568 | 0.683206024177 | 5.065047320051 |
| C | 1.554927528886 | -2.023626263095 | -2.894675366239 |
| H | 0.717162541065 | -2.547754409239 | -3.353678820759 |
| H | 1.518252296691 | -2.212477858024 | -1.820064478917 |
| H | 2.479657734471 | -2.455948000716 | -3.290820424309 |
| C | 1.608665324767 | -0.273952491079 | -4.686001206437 |
| H | 0.814899578150 | -0.792365846432 | -5.225340970274 |
| H | 2.562783465988 | -0.650696761925 | -5.069696159056 |
| H | 1.555644552242 | 0.790144646079 | -4.927910639510 |
| C | 2.771476627406 | 0.097369300654 | -2.519667715244 |
| H | 2.864083465292 | 1.160855878429 | -2.745853317197 |
| H | 3.669172795535 | -0.411057181979 | -2.885440573797 |
| H | 2.728136773364 | -0.020161659579 | -1.433546182213 |
| C | 1.554927528886 | -2.023626263095 | 2.894675366239 |
| H | 1.518252296691 | -2.212477858024 | 1.820064478917 |
| H | 0.717162541065 | -2.547754409239 | 3.353678820759 |
| H | 2.479657734471 | -2.455948000716 | 3.290820424309 |
| C | 2.771476627406 | 0.097369300654 | 2.519667715244 |
| H | 2.728136773364 | -0.020161659579 | 1.433546182213 |
| H | 3.669172795535 | -0.411057181979 | 2.885440573797 |
| H | 2.864083465292 | 1.160855878429 | 2.745853317197 |
| C | 1.608665324767 | -0.273952491079 | 4.686001206437 |
| H | 1.555644552242 | 0.790144646079 | 4.927910639510 |
| H | 2.562783465988 | -0.650696761925 | 5.069696159056 |
| H | 0.814899578150 | -0.792365846432 | 5.225340970274 |
| C | -1.573832885873 | 0.853674312961 | -4.572376805859 |
| H | -0.791015280184 | 0.597621424849 | -5.284739913292 |
| H | -1.505383508415 | 1.920610003378 | -4.352185939179 |
| H | -2.536830603568 | 0.683206024177 | -5.065047320051 |
| C | -2.637361055400 | 0.489798157877 | -2.365783927190 |
| H | -2.481846868869 | 1.524038242118 | -2.049051631298 |
| H | -2.699442689976 | -0.131959548163 | -1.472457976124 |
| H | -3.592258008500 | 0.436969803308 | -2.899520480323 |
| C | -1.741964334889 | -1.458437626948 | -3.624167384480 |
| H | -1.047131828462 | -1.818245872677 | -4.384993488556 |
| H | -2.754944514437 | -1.586491213443 | -4.019586350416 |
| H | -1.645924195281 | -2.082898676248 | -2.733651267324 |

65

13 $^1$A ($C_2$): $E_{tot}$(PBE0D/TZVP) = -2073.64977248

| | | | |
|---|---|---|---|
| Os | 0.000000000000 | 0.000000000000 | 0.039731076135 |
| N | 0.000000000000 | 0.000000000000 | -1.893476703082 |
| P | 0.000000000000 | 2.314371827578 | -0.239704722983 |
| P | 0.000000000000 | -2.314371827578 | -0.239704722983 |
| C | 0.049191089137 | 2.384585419632 | -2.046729096751 |
| H | 0.063317504387 | 3.290359229769 | -2.638878897608 |
| C | -0.049191089137 | -2.384585419632 | -2.046729096751 |
| H | -0.063317504387 | -3.290359229769 | -2.638878897608 |
| C | 0.032996411058 | 1.189226601849 | -2.638704140585 |
| H | 0.042939701221 | 1.078189119637 | -3.721455087696 |
| C | -0.032996411058 | -1.189226601849 | -2.638704140585 |
| H | -0.042939701221 | -1.078189119637 | -3.721455087696 |
| Cl | 0.000000000000 | 0.000000000000 | 2.352779718947 |
| C | -1.582160531915 | 3.230775486110 | 0.191503816407 |
| C | 1.582160531915 | -3.230775486110 | 0.191503816407 |
| C | 1.534424931937 | 3.260918703552 | 0.281136590555 |
| C | -1.534424931937 | -3.260918703552 | 0.281136590555 |
| C | -1.900159888829 | 3.023584717583 | 1.670742188891 |
| H | -1.926088328601 | 1.963534059509 | 1.924640863317 |
| H | -2.883348508966 | 3.456415579175 | 1.883091592030 |
| H | -1.176441311349 | 3.505058719102 | 2.327485236734 |
| C | -2.678519756021 | 2.544767741694 | -0.626330674660 |
| H | -2.675995745792 | 1.464961937230 | -0.455991947932 |
| H | -2.560157972488 | 2.721492658122 | -1.696698672753 |
| H | -3.650922826499 | 2.941584947238 | -0.318177297036 |
| C | -1.567498772496 | 4.717547366349 | -0.137255703333 |
| H | -1.283767256878 | 4.910635884944 | -1.174396409953 |
| H | -0.895209129619 | 5.274621253736 | 0.516693489872 |
| H | -2.573587594345 | 5.124663401352 | 0.009303970778 |
| C | 1.900159888829 | -3.023584717583 | 1.670742188891 |
| H | 1.176441311349 | -3.505058719102 | 2.327485236734 |
| H | 1.926088328601 | -1.963534059509 | 1.924640863317 |
| H | 2.883348508966 | -3.456415579175 | 1.883091592030 |
| C | 1.567498772496 | -4.717547366349 | -0.137255703333 |
| H | 0.895209129619 | -5.274621253736 | 0.516693489872 |
| H | 2.573587594345 | -5.124663401352 | 0.009303970778 |
| H | 1.283767256878 | -4.910635884944 | -1.174396409953 |
| C | 2.678519756021 | -2.544767741694 | -0.626330674660 |
| H | 2.560157972488 | -2.721492658122 | -1.696698672753 |
| H | 3.650922826499 | -2.941584947238 | -0.318177297036 |
| H | 2.675995745792 | -1.464961937230 | -0.455991947932 |
| C | 1.471666846904 | 3.562003997697 | 1.775182568048 |
| H | 1.205168964722 | 2.673288278772 | 2.352120317906 |
| H | 0.755754923940 | 4.353878197085 | 2.001810015031 |
| H | 2.455784196630 | 3.903287860406 | 2.112434696684 |
| C | 2.697288243269 | 2.301499887527 | 0.019631194253 |
| H | 2.611018120856 | 1.399012562744 | 0.626595109830 |
| H | 3.637541886548 | 2.806395336020 | 0.265835303505 |
| H | 2.738323931309 | 1.997893038950 | -1.029599725924 |
| C | 1.782378208287 | 4.539495719977 | -0.512334931924 |
| H | 1.902007976816 | 4.332052220944 | -1.577457775036 |
| H | 2.713915186706 | 4.996470562594 | -0.162143661213 |
| H | 0.990359805828 | 5.276763295849 | -0.391931184586 |
| C | -1.782378208287 | -4.539495719977 | -0.512334931924 |
| H | -0.990359805828 | -5.276763295849 | -0.391931184586 |
| H | -1.902007976816 | -4.332052220944 | -1.577457775036 |
| H | -2.713915186706 | -4.996470562594 | -0.162143661213 |
| C | -2.697288243269 | -2.301499887527 | 0.019631194253 |
| H | -2.738323931309 | -1.997893038950 | -1.029599725924 |
| H | -2.611018120856 | -1.399012562744 | 0.626595109830 |
| H | -3.637541886548 | -2.806395336020 | 0.265835303505 |
| C | -1.471666846904 | -3.562003997697 | 1.775182568048 |
| H | -0.755754923940 | -4.353878197085 | 2.001810015031 |
| H | -2.455784196630 | -3.903287860406 | 2.112434696684 |
| H | -1.205168964722 | -2.673288278772 | 2.352120317906 |

65

13 $^3A''$ ($C_s$): $E_{tot}$(PBE0D/TZVP) = -2073.64995876

| | | | |
|---|---|---|---|
| Os | -0.043458612535 | -0.093358317372 | 0.000000000000 |
| N | 0.204306864891 | 1.949037258266 | 0.000000000000 |
| P | 0.036586366680 | 0.298982138533 | 2.342234233831 |
| P | 0.036586366680 | 0.298982138533 | -2.342234233831 |
| C | 0.195462398748 | 2.071584413787 | 2.381774005377 |
| H | 0.263284616920 | 2.661417741834 | 3.285539480597 |
| C | 0.195462398748 | 2.071584413787 | -2.381774005377 |
| H | 0.263284616920 | 2.661417741834 | -3.285539480597 |
| C | 0.266966570830 | 2.654138131866 | 1.170887401714 |
| H | 0.380656825746 | 3.733762168885 | 1.074093447363 |
| C | 0.266966570830 | 2.654138131866 | -1.170887401714 |
| H | 0.380656825746 | 3.733762168885 | -1.074093447363 |
| Cl | -0.534684006630 | -2.299359051198 | 0.000000000000 |
| C | -1.527106737176 | -0.081950150991 | 3.307508206274 |
| C | 1.577264216816 | -0.378177505894 | -3.173700015275 |
| C | 1.577264216816 | -0.378177505894 | 3.173700015275 |
| C | -1.527106737176 | -0.081950150991 | -3.307508206274 |
| C | -1.629642684779 | -1.569935173474 | 3.622009047216 |
| H | -1.478245481889 | -2.182159281730 | 2.730498052049 |
| H | -2.631503752360 | -1.782230614132 | 4.008680081636 |
| H | -0.913265015904 | -1.878061063238 | 4.385363436786 |
| C | -2.676073315649 | 0.312200341584 | 2.378123891519 |
| H | -2.687219109635 | -0.301564312396 | 1.476388368244 |
| H | -2.599042578698 | 1.357572091087 | 2.070382653339 |
| H | -3.624029162395 | 0.179442937791 | 2.910270889644 |
| C | -1.642364385387 | 0.740061698156 | 4.588151690920 |
| H | -1.636000771913 | 1.810365589027 | 4.374772354855 |
| H | -0.850867417801 | 0.525381977808 | 5.304873418007 |
| H | -2.597054250540 | 0.506120498922 | 5.070460461320 |
| C | 1.694602581860 | -1.878735581805 | -2.918978664594 |
| H | 0.896839675789 | -2.451217475298 | -3.390822167542 |
| H | 1.678339262813 | -2.096586153737 | -1.850167710092 |
| H | 2.646345127689 | -2.232322316955 | -3.328769365739 |
| C | 1.644332240921 | -0.088044039086 | -4.667586012507 |
| H | 0.904445419923 | -0.658699244573 | -5.230594772886 |
| H | 2.631972671576 | -0.376336122465 | -5.042368776179 |
| H | 1.506680605060 | 0.973423923133 | -4.886433473545 |
| C | 2.746924734769 | 0.313445953137 | -2.471921708868 |
| H | 2.766408269112 | 1.385161969418 | -2.674280140203 |
| H | 3.683415816012 | -0.125413516584 | -2.830190215166 |
| H | 2.689017330144 | 0.170218192919 | -1.389462693942 |
| C | 1.694602581860 | -1.878735581805 | 2.918978664594 |
| H | 1.678339262813 | -2.096586153737 | 1.850167710092 |
| H | 0.896839675789 | -2.451217475298 | 3.390822167542 |
| H | 2.646345127689 | -2.232322316955 | 3.328769365739 |
| C | 2.746924734769 | 0.313445953137 | 2.471921708868 |
| H | 2.689017330144 | 0.170218192919 | 1.389462693942 |
| H | 3.683415816012 | -0.125413516584 | 2.830190215166 |
| H | 2.766408269112 | 1.385161969418 | 2.674280140203 |
| C | 1.644332240921 | -0.088044039086 | 4.667586012507 |
| H | 1.506680605060 | 0.973423923133 | 4.886433473545 |
| H | 2.631972671576 | -0.376336122465 | 5.042368776179 |
| H | 0.904445419923 | -0.658699244573 | 5.230594772886 |
| C | -1.642364385387 | 0.740061698156 | -4.588151690920 |
| H | -0.850867417801 | 0.525381977808 | -5.304873418007 |
| H | -1.636000771913 | 1.810365589027 | -4.374772354855 |
| H | -2.597054250540 | 0.506120498922 | -5.070460461320 |
| C | -2.676073315649 | 0.312200341584 | -2.378123891519 |
| H | -2.599042578698 | 1.357572091087 | -2.070382653339 |
| H | -2.687219109635 | -0.301564312396 | -1.476388368244 |
| H | -3.624029162395 | 0.179442937791 | -2.910270889644 |
| C | -1.629642684779 | -1.569935173474 | -3.622009047216 |
| H | -0.913265015904 | -1.878061063238 | -4.385363436786 |
| H | -2.631503752360 | -1.782230614132 | -4.008680081636 |
| H | -1.478245481889 | -2.182159281730 | -2.730498052049 |

65

13 $^{3}$B ($C_2$): $E_{tot}$(PBE0D/TZVP) = -2073.66707021

| | | | |
|---|---|---|---|
| Os | 0.000000000000 | 0.000000000000 | 0.043430925012 |
| N | 0.000000000000 | 0.000000000000 | -1.970293521730 |
| P | 0.000000000000 | 2.324728405854 | -0.267534793643 |
| P | 0.000000000000 | -2.324728405854 | -0.267534793643 |
| C | 0.039129264870 | 2.384003498999 | -2.062351607177 |
| H | 0.054085448584 | 3.292297344719 | -2.650282432114 |
| C | -0.039129264870 | -2.384003498999 | -2.062351607177 |
| H | -0.054085448584 | -3.292297344719 | -2.650282432114 |
| C | 0.027306105901 | 1.183706878627 | -2.670492557356 |
| H | 0.038821081035 | 1.100832960289 | -3.757204500725 |
| C | -0.027306105901 | -1.183706878627 | -2.670492557356 |
| H | -0.038821081035 | -1.100832960289 | -3.757204500725 |
| Cl | 0.000000000000 | 0.000000000000 | 2.406318429581 |
| C | -1.541746430595 | 3.271384638141 | 0.216441506477 |
| C | 1.541746430595 | -3.271384638141 | 0.216441506477 |
| C | 1.579507416156 | 3.180251124587 | 0.265595938119 |
| C | -1.579507416156 | -3.180251124587 | 0.265595938119 |
| C | -1.797534823448 | 3.138490795372 | 1.715823247630 |
| H | -1.751666505089 | 2.097645354047 | 2.040613846761 |
| H | -2.795715337933 | 3.528855464857 | 1.939738462796 |
| H | -1.081819165519 | 3.702915756343 | 2.311771172195 |
| C | -2.678788620805 | 2.564284058005 | -0.523876349283 |
| H | -2.725975274585 | 1.504426229145 | -0.258250779523 |
| H | -2.568688915059 | 2.637861335712 | -1.606882945152 |
| H | -3.629985665252 | 3.024017132270 | -0.238622346051 |
| C | -1.513698585899 | 4.739692625439 | -0.187555201023 |
| H | -1.284017290350 | 4.871399465816 | -1.247455736238 |
| H | -0.789355724900 | 5.307575213871 | 0.398169408224 |
| H | -2.498359288848 | 5.183143387291 | -0.005597163482 |
| C | 1.797534823448 | -3.138490795372 | 1.715823247630 |
| H | 1.081819165519 | -3.702915756343 | 2.311771172195 |
| H | 1.751666505089 | -2.097645354047 | 2.040613846761 |
| H | 2.795715337933 | -3.528855464857 | 1.939738462796 |
| C | 1.513698585899 | -4.739692625439 | -0.187555201023 |
| H | 0.789355724900 | -5.307575213871 | 0.398169408224 |
| H | 2.498359288848 | -5.183143387291 | -0.005597163482 |
| H | 1.284017290350 | -4.871399465816 | -1.247455736238 |
| C | 2.678788620805 | -2.564284058005 | -0.523876349283 |
| H | 2.568688915059 | -2.637861335712 | -1.606882945152 |
| H | 3.629985665252 | -3.024017132270 | -0.238622346051 |
| H | 2.725975274585 | -1.504426229145 | -0.258250779523 |
| C | 1.542908341313 | 3.504648108568 | 1.754759162919 |
| H | 1.209283018275 | 2.647615496590 | 2.344796440615 |
| H | 0.891911424882 | 4.353871647193 | 1.968396614989 |
| H | 2.550895086427 | 3.774261374465 | 2.086639314762 |
| C | 2.669402941024 | 2.134694162481 | 0.015750375397 |
| H | 2.542249090562 | 1.268913607923 | 0.672114506441 |
| H | 3.649909359553 | 2.574154198799 | 0.226789041011 |
| H | 2.668666865612 | 1.792262607458 | -1.022555934008 |
| C | 1.905086687998 | 4.427336493621 | -0.548098976989 |
| H | 2.007321950270 | 4.194571514591 | -1.609619451216 |
| H | 2.860385785987 | 4.838303679814 | -0.204978564955 |
| H | 1.153094034854 | 5.208387555009 | -0.438584757789 |
| C | -1.905086687998 | -4.427336493621 | -0.548098976989 |
| H | -1.153094034854 | -5.208387555009 | -0.438584757789 |
| H | -2.007321950270 | -4.194571514591 | -1.609619451216 |
| H | -2.860385785987 | -4.838303679814 | -0.204978564955 |
| C | -2.669402941024 | -2.134694162481 | 0.015750375397 |
| H | -2.668666865612 | -1.792262607458 | -1.022555934008 |
| H | -2.542249090562 | -1.268913607923 | 0.672114506441 |
| H | -3.649909359553 | -2.574154198799 | 0.226789041011 |
| C | -1.542908341313 | -3.504648108568 | 1.754759162919 |
| H | -0.891911424882 | -4.353871647193 | 1.968396614989 |
| H | -2.550895086427 | -3.774261374465 | 2.086639314762 |
| H | -1.209283018275 | -2.647615496590 | 2.344796440615 |

29
13,Me $^1A'$ ($C_s$): $E_{tot}$(PBE0D/TZVP) = -1602.27077829

| | | | |
|---|---|---|---|
| Os | 0.224551836699 | 0.082754872870 | 0.000000000000 |
| N | -1.693420776872 | -0.163943476167 | 0.000000000000 |
| P | -0.050223458425 | 0.045943951425 | 2.314665703588 |
| P | -0.050223458425 | 0.045943951425 | -2.314665703588 |
| C | -1.834475218600 | -0.232394087097 | 2.385752352981 |
| H | -2.419207927887 | -0.331042494892 | 3.290957045670 |
| C | -1.834475218600 | -0.232394087097 | -2.385752352981 |
| H | -2.419207927887 | -0.331042494892 | -3.290957045670 |
| C | -2.422955586851 | -0.298437734195 | 1.189504560211 |
| H | -3.494884077680 | -0.452289678696 | 1.079416470417 |
| C | -2.422955586851 | -0.298437734195 | -1.189504560211 |
| H | -3.494884077680 | -0.452289678696 | -1.079416470417 |
| Cl | 2.510168699932 | -0.249599354312 | 0.000000000000 |
| C | 0.654492258145 | -1.388628178012 | 3.298778366664 |
| C | 0.202806336452 | 1.689444410385 | -3.185798142593 |
| C | 0.202806336452 | 1.689444410385 | 3.185798142593 |
| C | 0.654492258145 | -1.388628178012 | -3.298778366664 |
| H | 1.704211728957 | -1.206864559326 | 3.531363942762 |
| H | 0.583899711779 | -2.249743573405 | 2.633995635303 |
| H | 0.097283954357 | -1.612841659035 | 4.209709590451 |
| H | 1.216117142862 | 2.034586092376 | -2.977991937394 |
| H | 0.017672582530 | 1.678044775104 | -4.261621002867 |
| H | -0.493378998346 | 2.381796869185 | -2.710857987496 |
| H | 1.216117142862 | 2.034586092376 | 2.977991937394 |
| H | -0.493378998346 | 2.381796869185 | 2.710857987496 |
| H | 0.017672582530 | 1.678044775104 | 4.261621002867 |
| H | 0.097283954357 | -1.612841659035 | -4.209709590451 |
| H | 0.583899711779 | -2.249743573405 | -2.633995635303 |
| H | 1.704211728957 | -1.206864559326 | -3.531363942762 |

29
13,Me $^1A$ ($C_2$): $E_{tot}$(PBE0D/TZVP) = -1602.27012880

| | | | |
|---|---|---|---|
| Os | 0.000000000000 | 0.000000000000 | 0.229231499142 |
| N | 0.000000000000 | 0.000000000000 | -1.703976280075 |
| P | 0.000000000000 | 2.314371827578 | -0.050204299976 |
| P | 0.000000000000 | -2.314371827578 | -0.050204299976 |
| C | 0.049191089137 | 2.384585419632 | -1.857228673744 |
| H | 0.063317504387 | 3.290359229769 | -2.449378474601 |
| C | -0.049191089137 | -2.384585419632 | -1.857228673744 |
| H | -0.063317504387 | -3.290359229769 | -2.449378474601 |
| C | 0.032996411058 | 1.189226601849 | -2.449203717578 |
| H | 0.042939701221 | 1.078189119637 | -3.531954664689 |
| C | -0.032996411058 | -1.189226601849 | -2.449203717578 |
| H | -0.042939701221 | -1.078189119637 | -3.531954664689 |
| Cl | 0.000000000000 | 0.000000000000 | 2.542280141954 |
| C | -1.582160531915 | 3.230775486110 | 0.381004239414 |
| C | 1.582160531915 | -3.230775486110 | 0.381004239414 |
| C | 1.534424931937 | 3.260918703552 | 0.470637013562 |
| C | -1.534424931937 | -3.260918703552 | 0.470637013562 |
| H | -1.809250775855 | 3.082816060583 | 1.437360472688 |
| H | -2.363550813247 | 2.741848341959 | -0.201877638174 |
| H | -1.571649730375 | 4.296620567994 | 0.145321333452 |
| H | 1.809250775855 | -3.082816060583 | 1.437360472688 |
| H | 1.571649730375 | -4.296620567994 | 0.145321333452 |
| H | 2.363550813247 | -2.741848341959 | -0.201877638174 |
| H | 1.489552946211 | 3.476194472628 | 1.538878814455 |
| H | 2.362981685483 | 2.577319064841 | 0.284310675734 |
| H | 1.711841289168 | 4.175770404777 | -0.097110382870 |
| H | -1.711841289168 | -4.175770404777 | -0.097110382870 |
| H | -2.362981685483 | -2.577319064841 | 0.284310675734 |
| H | -1.489552946211 | -3.476194472628 | 1.538878814455 |

29

13,Me $^3$A″ (C$_s$): $E_{tot}$(PBE0D/TZVP) = -1602.26878780

| | | | |
|---|---|---|---|
| Os | 0.283054454091 | 0.014455569231 | 0.000000000000 |
| N | -1.772238879854 | -0.077938860412 | 0.000000000000 |
| P | -0.117114232946 | 0.028712285266 | 2.342234233831 |
| P | -0.117114232946 | 0.028712285266 | -2.342234233831 |
| C | -1.891650271201 | -0.106868940332 | 2.381774005377 |
| H | -2.484593175604 | -0.137232080344 | 3.285539480597 |
| C | -1.891650271201 | -0.106868940332 | -2.381774005377 |
| H | -2.484593175604 | -0.137232080344 | -3.285539480597 |
| C | -2.478020321599 | -0.132400197056 | 1.170887401714 |
| H | -3.561612878774 | -0.198284227033 | 1.074093447363 |
| C | -2.478020321599 | -0.132400197056 | -1.170887401714 |
| H | -3.561612878774 | -0.198284227033 | -1.074093447363 |
| Cl | 2.539857398269 | -0.106300782954 | 0.000000000000 |
| C | 0.516439669272 | -1.450765658211 | 3.307508206274 |
| C | 0.296735738916 | 1.659957706020 | -3.173700015275 |
| C | 0.296735738916 | 1.659957706020 | 3.173700015275 |
| C | 0.516439669272 | -1.450765658211 | -3.307508206274 |
| H | 1.578515150244 | -1.347586235667 | 3.532511956827 |
| H | 0.374425645394 | -2.304566940246 | 2.645273891728 |
| H | -0.049747672103 | -1.628984319496 | 4.223301136578 |
| H | 1.340015060628 | 1.919341927419 | -2.991766131241 |
| H | 0.083680053059 | 1.673082928634 | -4.244556292320 |
| H | -0.327018642239 | 2.401038240980 | -2.673440680934 |
| H | 1.340015060628 | 1.919341927419 | 2.991766131241 |
| H | -0.327018642239 | 2.401038240980 | 2.673440680934 |
| H | 0.083680053059 | 1.673082928634 | 4.244556292320 |
| H | -0.049747672103 | -1.628984319496 | -4.223301136578 |
| H | 0.374425645394 | -2.304566940246 | -2.645273891728 |
| H | 1.578515150244 | -1.347586235667 | -3.532511956827 |

29

13,Me $^3$B (C$_2$): $E_{tot}$(PBE0D/TZVP) = -1602.28318619

| | | | |
|---|---|---|---|
| Os | 0.000000000000 | 0.000000000000 | 0.236343998081 |
| N | 0.000000000000 | 0.000000000000 | -1.777380448661 |
| P | 0.000000000000 | 2.324728405854 | -0.074621720574 |
| P | 0.000000000000 | -2.324728405854 | -0.074621720574 |
| C | 0.039129264870 | 2.384003498999 | -1.869438534108 |
| H | 0.054085448584 | 3.292297344719 | -2.457369359045 |
| C | -0.039129264870 | -2.384003498999 | -1.869438534108 |
| H | -0.054085448584 | -3.292297344719 | -2.457369359045 |
| C | 0.027306105901 | 1.183706878627 | -2.477579484287 |
| H | 0.038821081035 | 1.100832960289 | -3.564291427656 |
| C | -0.027306105901 | -1.183706878627 | -2.477579484287 |
| H | -0.038821081035 | -1.100832960289 | -3.564291427656 |
| Cl | 0.000000000000 | 0.000000000000 | 2.599231502650 |
| C | -1.541746430595 | 3.271384638141 | 0.409354579546 |
| C | 1.541746430595 | -3.271384638141 | 0.409354579546 |
| C | 1.579507416156 | 3.180251124587 | 0.458509011188 |
| C | -1.579507416156 | -3.180251124587 | 0.458509011188 |
| H | -1.724457840540 | 3.176457651367 | 1.480373279481 |
| H | -2.352567007802 | 2.767153831698 | -0.118563343195 |
| H | -1.521651154914 | 4.323374696870 | 0.119905415116 |
| H | 1.724457840540 | -3.176457651367 | 1.480373279481 |
| H | 1.521651154914 | -4.323374696870 | 0.119905415116 |
| H | 2.352567007802 | -2.767153831698 | -0.118563343195 |
| H | 1.553326381595 | 3.412307499932 | 1.523777300685 |
| H | 2.356003051620 | 2.435344480620 | 0.280506638880 |
| H | 1.812501221534 | 4.072700954451 | -0.123794258966 |
| H | -1.812501221534 | -4.072700954451 | -0.123794258966 |
| H | -2.356003051620 | -2.435344480620 | 0.280506638880 |
| H | -1.553326381595 | -3.412307499932 | 1.523777300685 |

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