Supplementary Information

Accessing Multimetallic Complexes with a Phosphorus (I) Zwitterion

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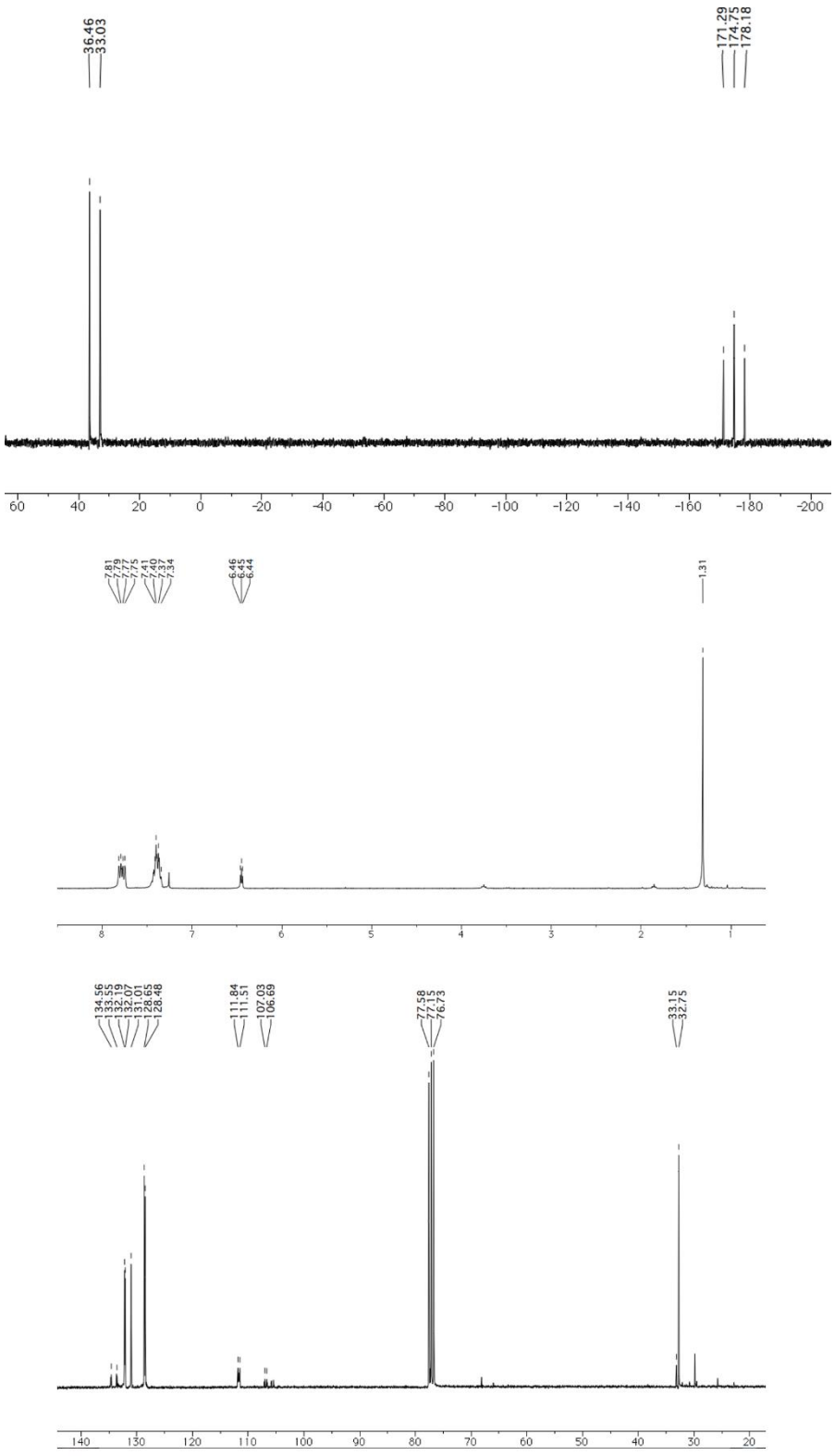

Figure 1. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of **1**

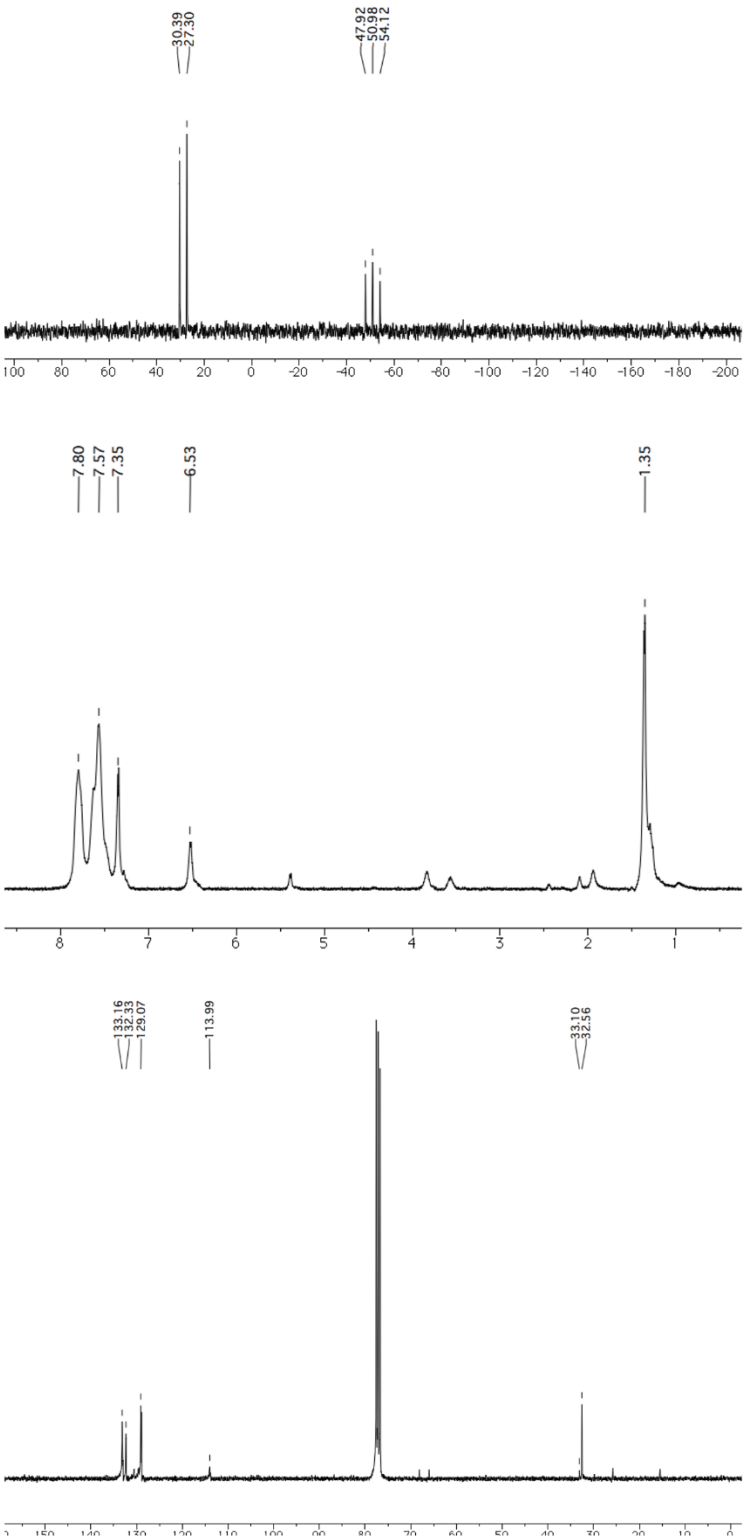

Figure 2. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of **2** in $CDCl_3$

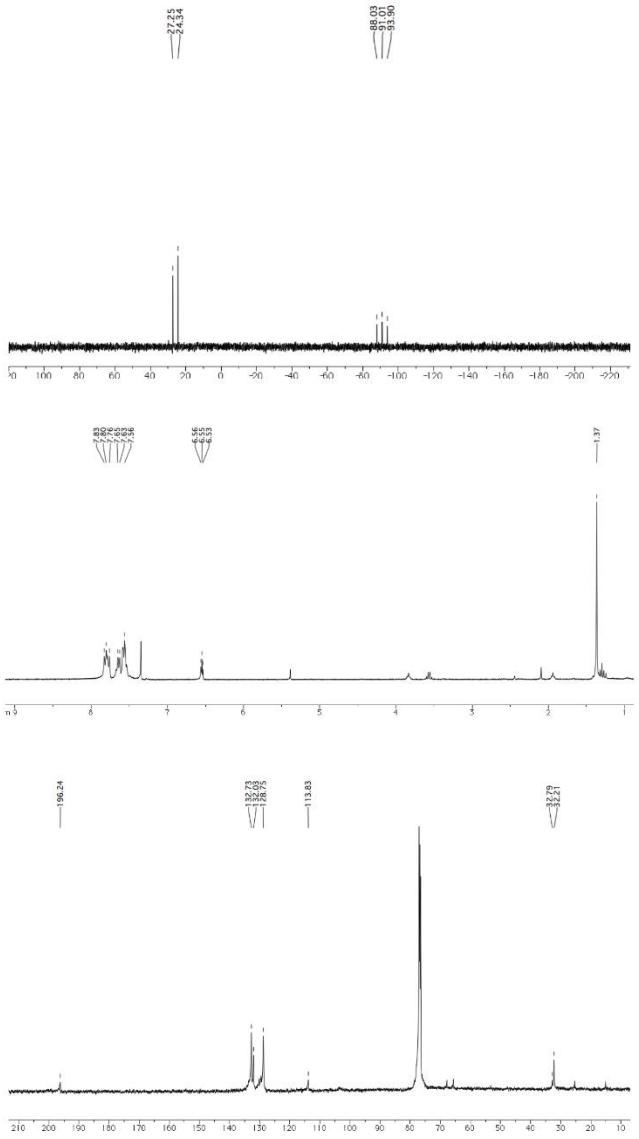

Figure 3. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of 3 in $CDCl_3$

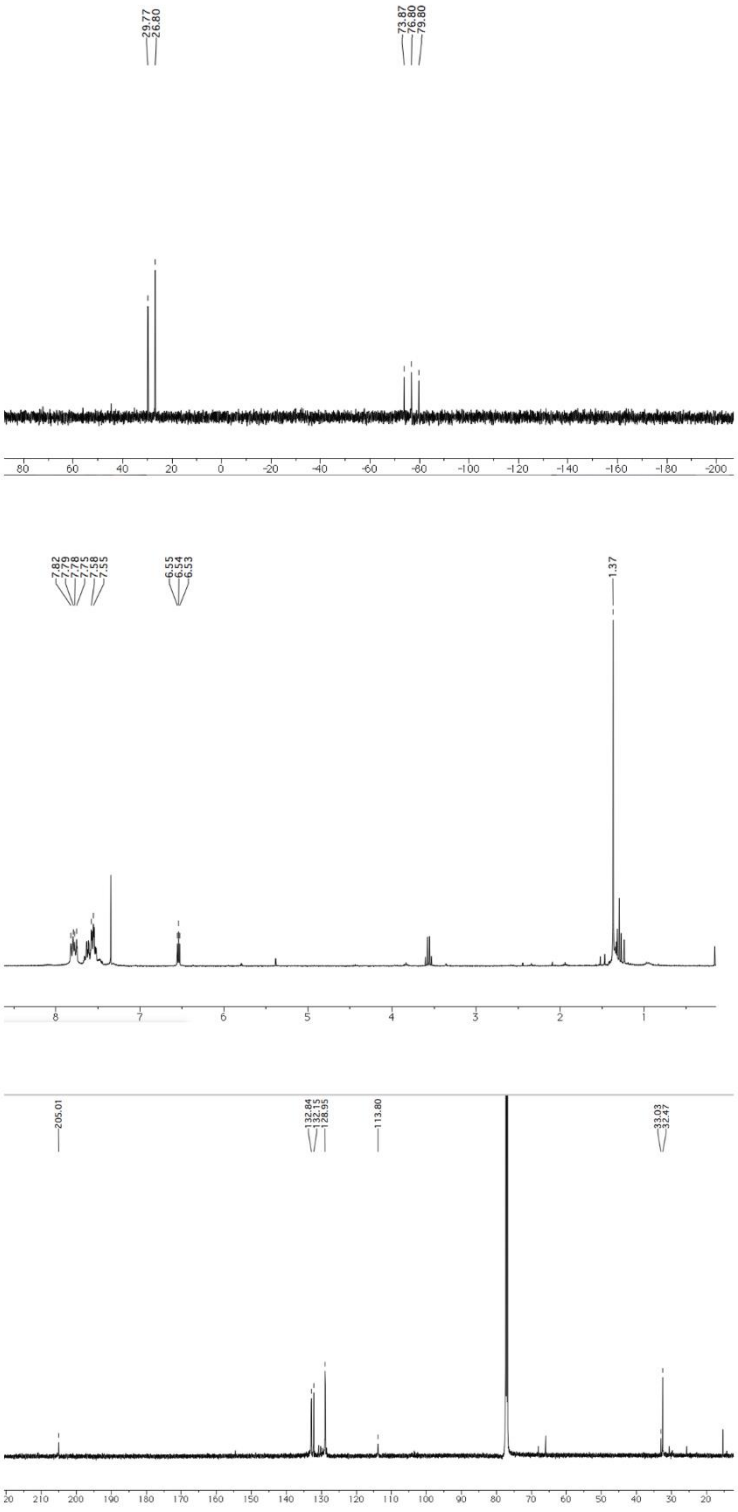

Figure 4. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of **4** in $CDCl_3$

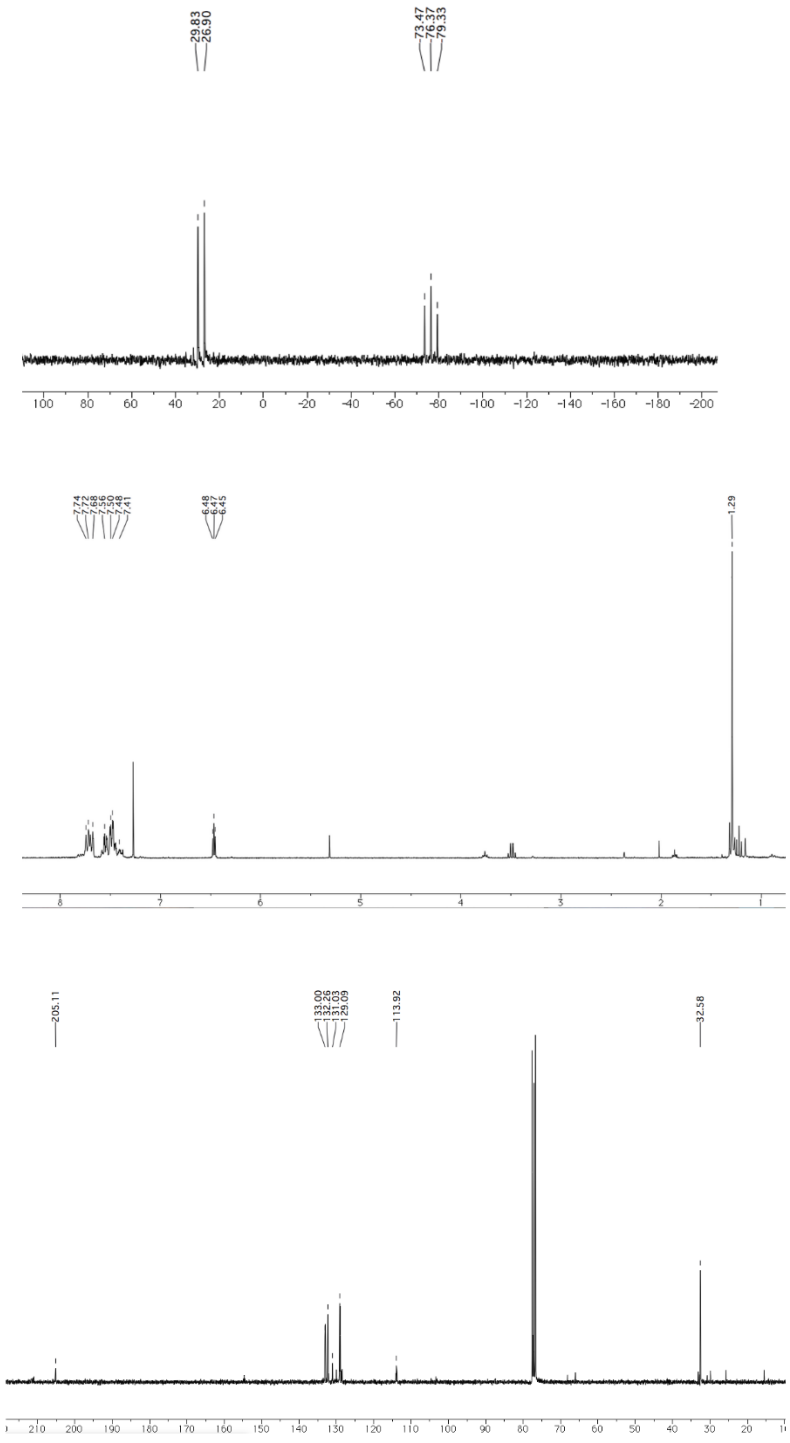

Figure 5. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of **5** in $CDCl_3$

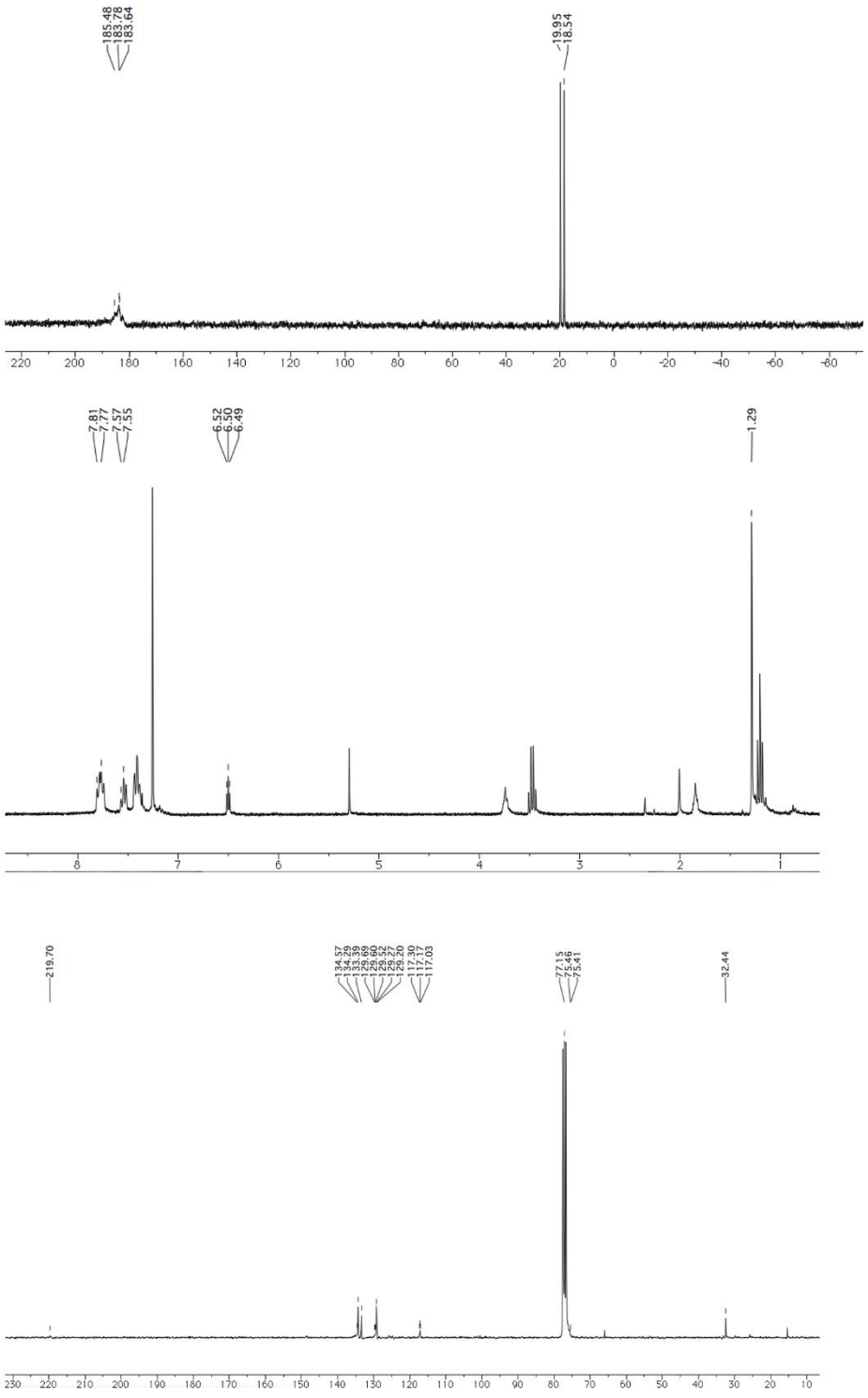

Figure 6. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle, Et_2O and THF also present in the spectrum), and ^{13}C (bottom) NMR Spectra of **6** in $CDCl_3$

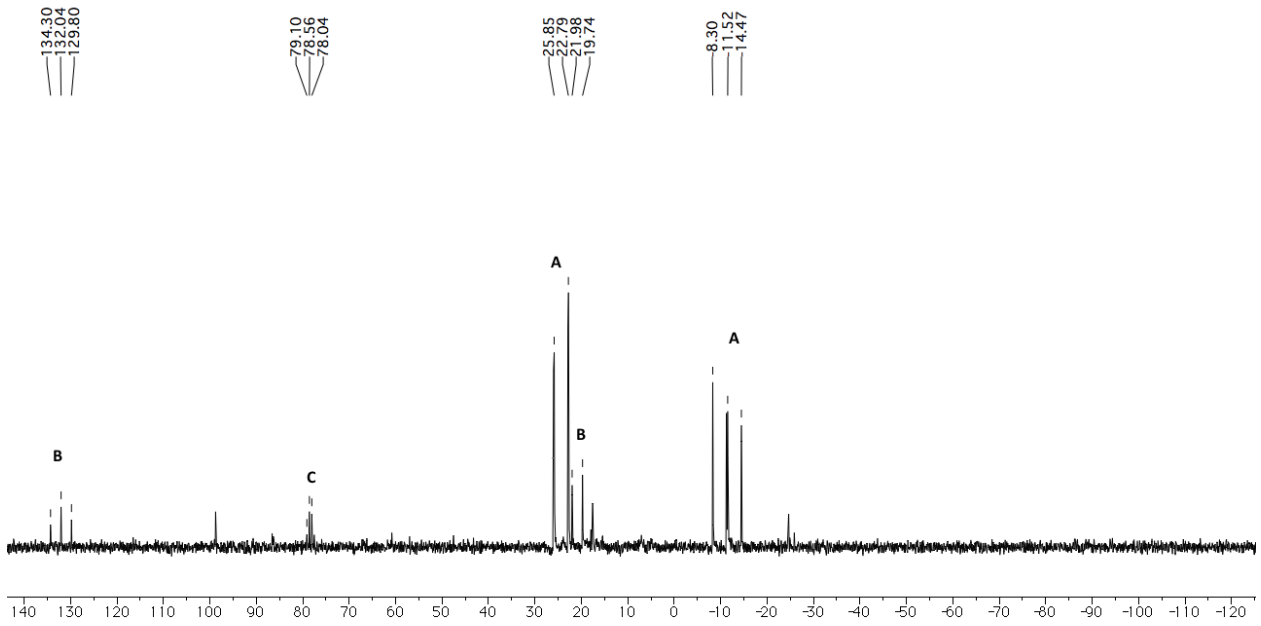

Figure 7. $^{31}P\{^{1}H\}$ of the reaction between **1**, Fe_2CO_9 and Me_3NO. All of **1** has been consumed to produce at least 3 species, labelled A, B, and C. A is likely the coordination molecule **7**, while **B** could be the bimetallic complex which would be analogous to the compounds **6** and **8** reported in this work.

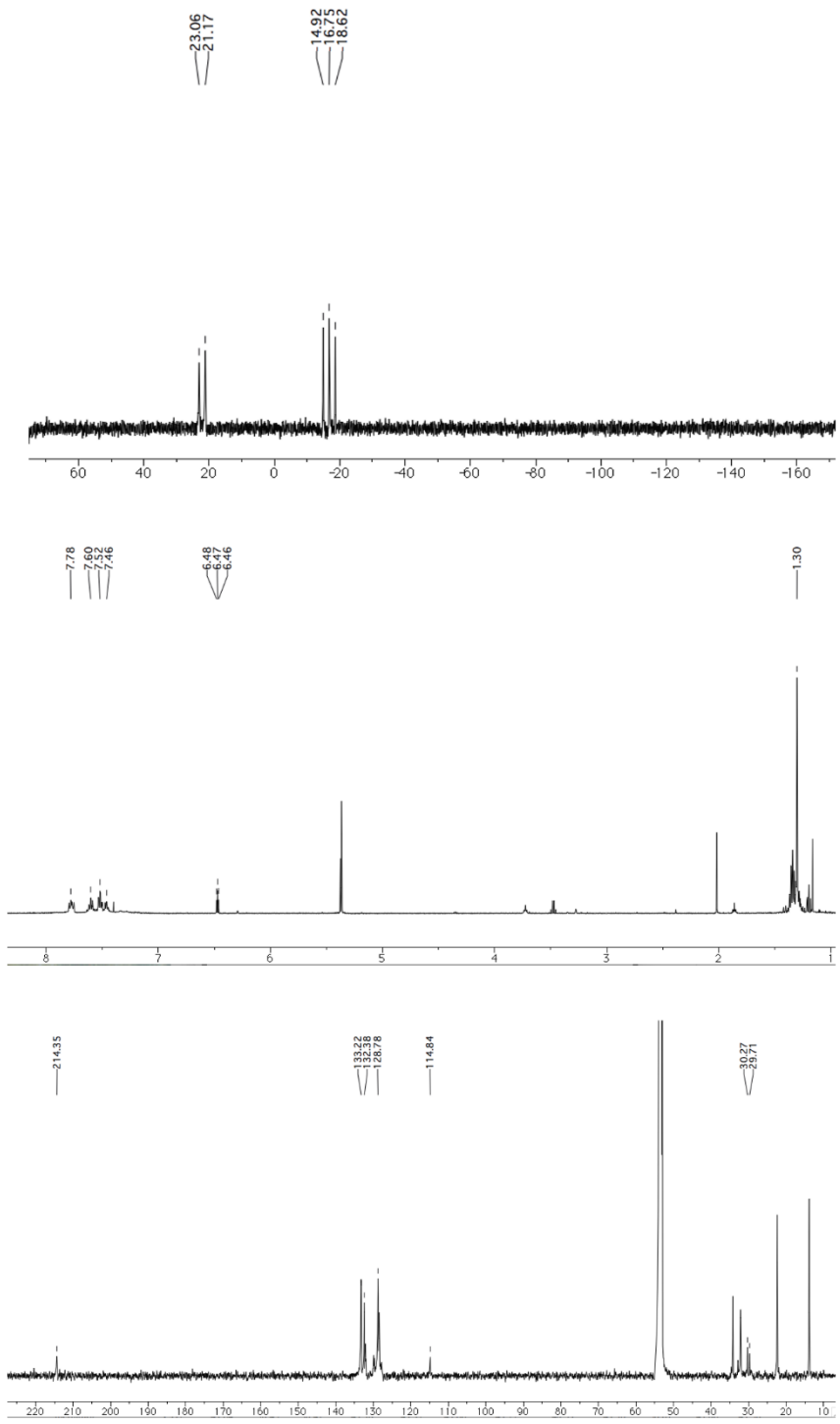

Figure 8. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of **7** in CD_2Cl_2, hexanes is present in the sample as well.

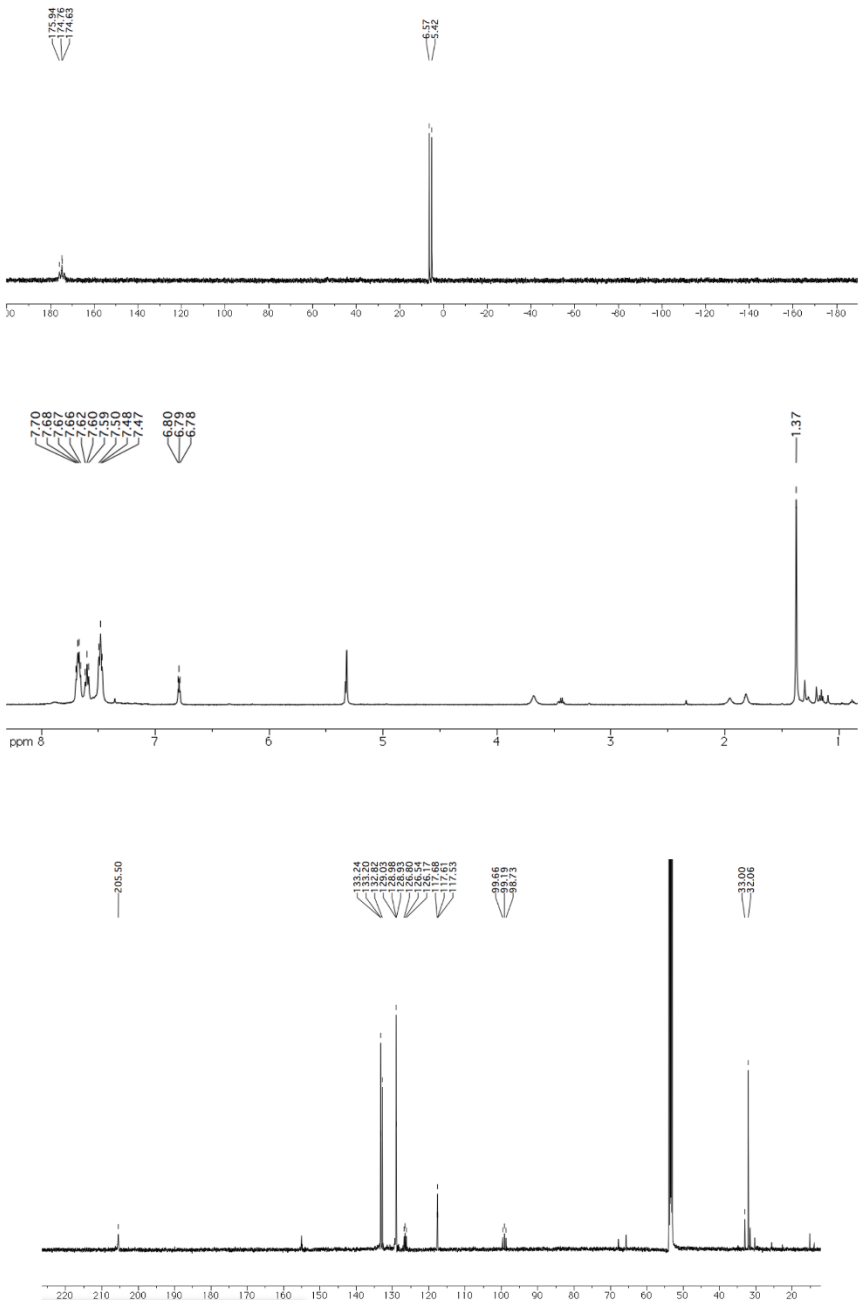

Figure 9. $^{31}P\{^{1}H\}$ (top), ^{1}H (middle), and ^{13}C (bottom) NMR Spectra of **8** in CD_2Cl_2

Computational Details

Calculations were performed with the Gaussian 09 suite of programs[1] using Compute Canada's Shared Hierarchical Academic Research Computing Network (SHARCNET). Model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method[2–4] in conjunction with the TZVP basis sets for all atoms.[5,6] The default Stuttgart-Dresden (SDD) quasi-relativistic effective core potentials were used for transition element atoms.[7,8] Geometry optimizations were started using models in which the relevant non-hydrogen atoms were placed in positions found experimentally using X-ray crystallography and the hydrogen atoms were placed in geometrically appropriate positions using Gaussview.[9] Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical and vibrational information. Natural bond orbital (NBO) analyses[10] to determine orbital contributions, Wiberg Bond Indicies and orbital energies were obtained using the routine included in the Gaussian distributions.[11] Visualizations of the Kohn-Sham orbitals and optimized geometries were made using Visual Molecular Dynamics (VMD).[12]

L

1\1\GINC-ORC333\FOpt\RPBE1PBE\TZVP\C6H9P3\BINDERJ\11-Oct-2017\0\\# PBE
1PBE/TZVP scf=tight opt freq pop=(full,nbo6read) test\\Optimization, f
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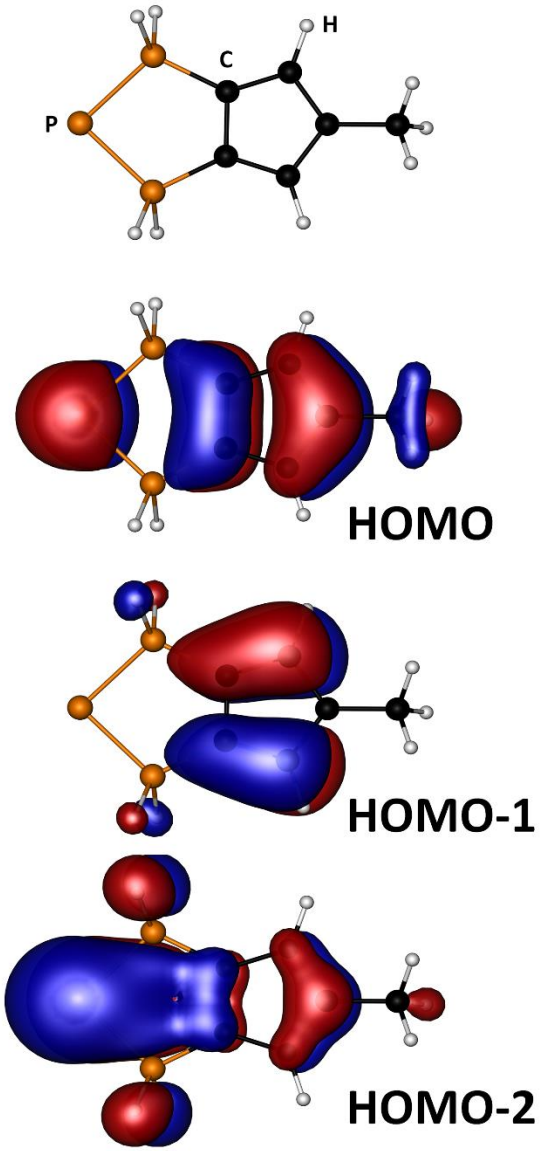

Figure 10. Frontier orbital depictions and energies for **L**.

$LCr(CO)_5$

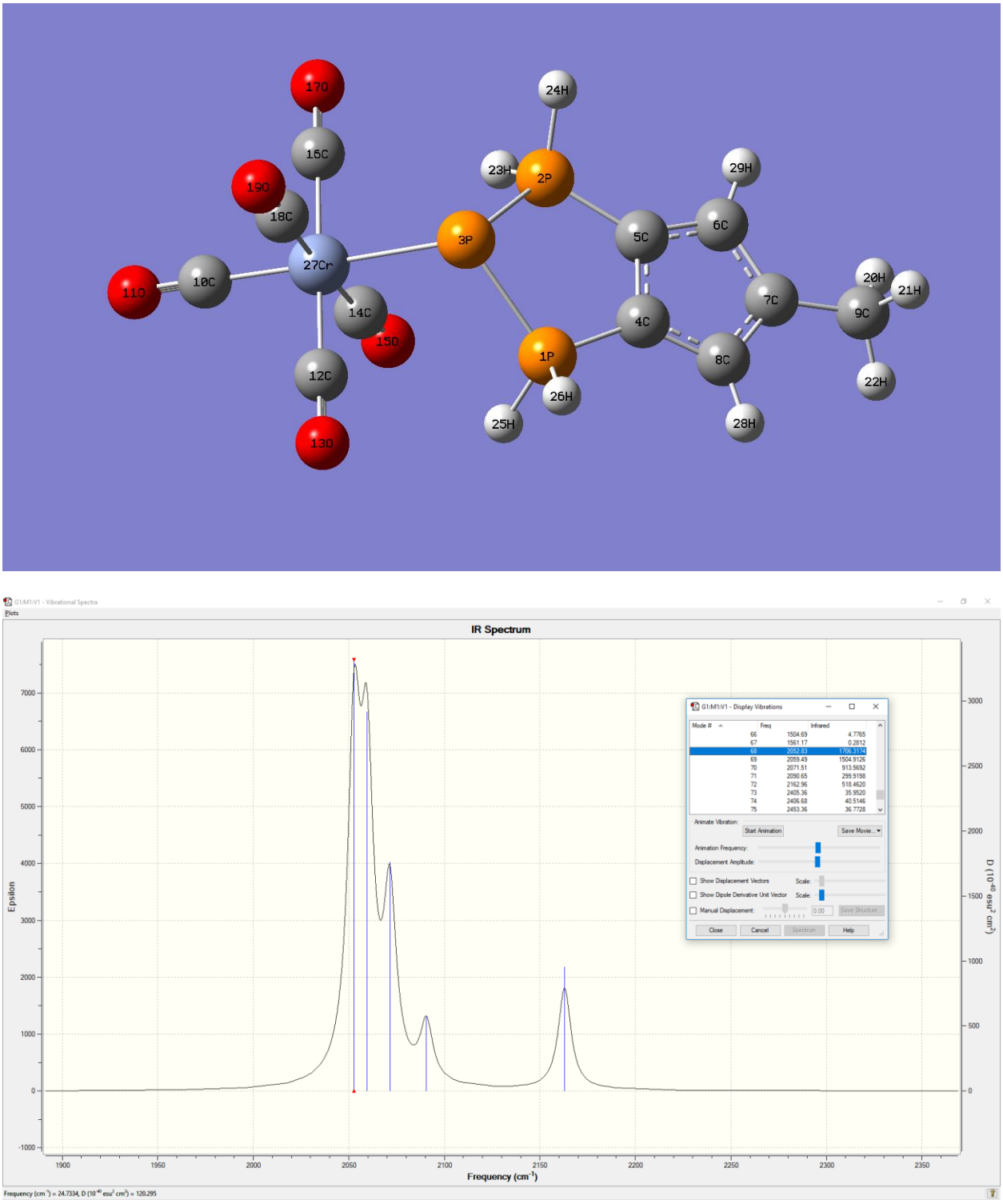

Figure 11. Optimized geometry and carbonyl region of the calculated IR spectrum for $LCr(CO)_5$.

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\Optimization, frequency test and NBO6 analysis for SPHOSCr(CO)5\\0,1\

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,5.8117256851,10.1322234556\O,4.5853075736,5.8200087028,9.0994845478\C

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Thermal correction to Gibbs Free Energy= 0.118194

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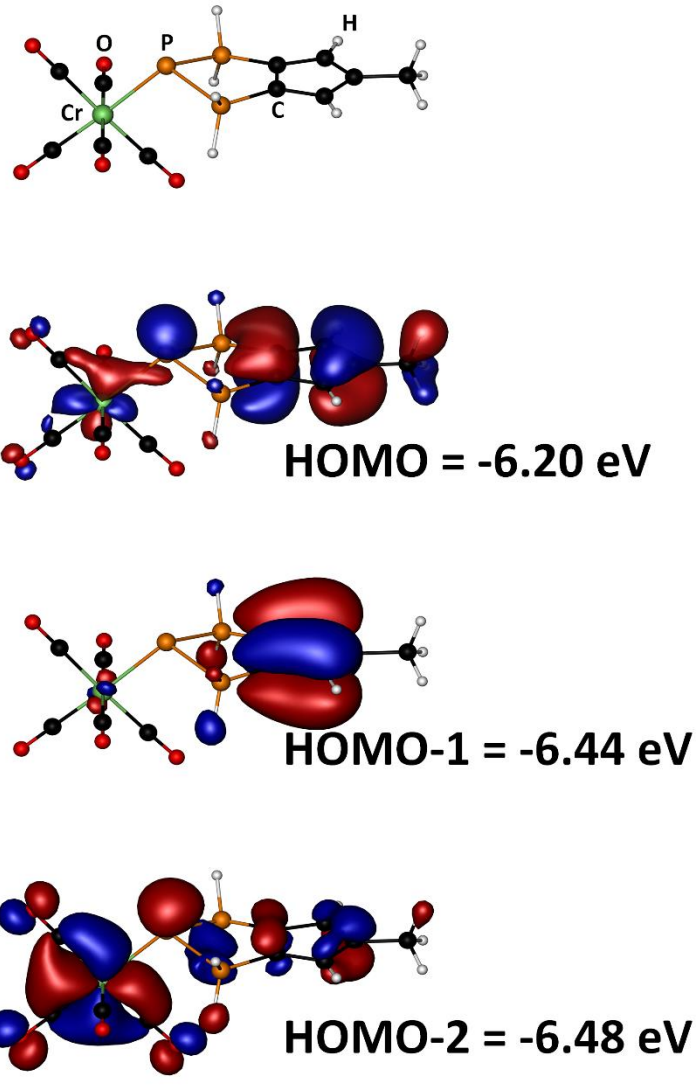
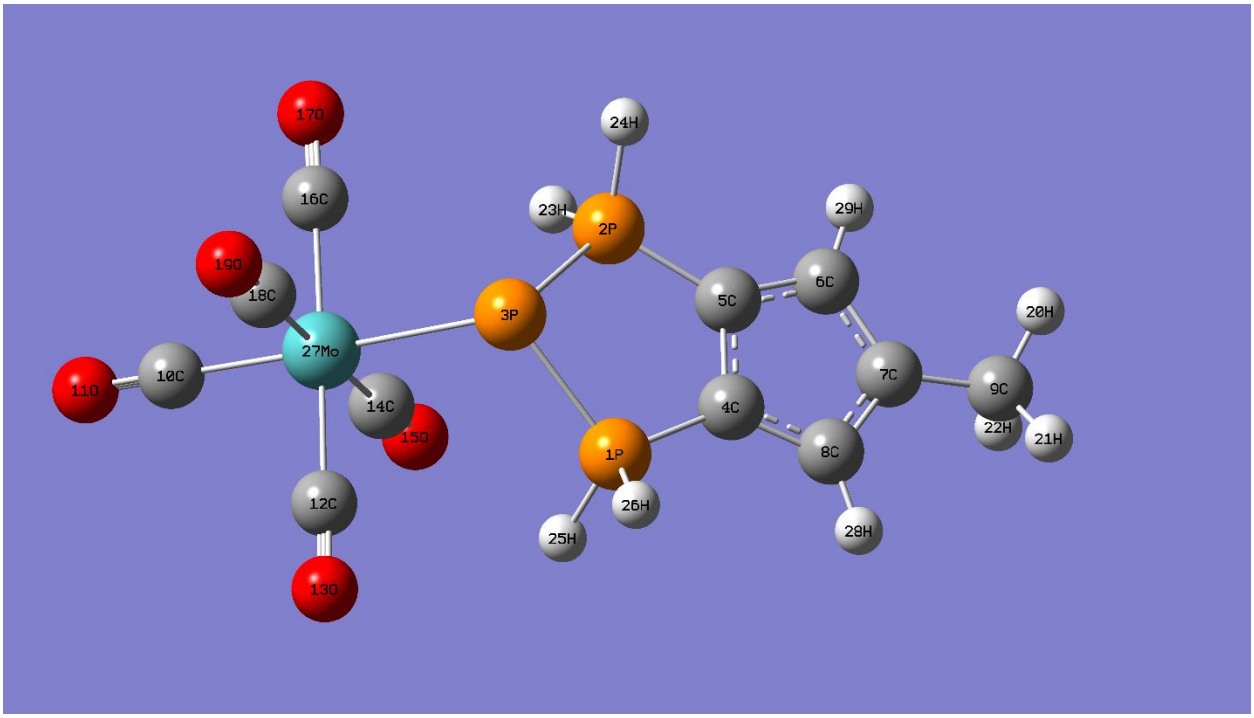


Figure 12. Frontier orbital depictions and energies for $LCr(CO)_5$.

$LMo(CO)_5$



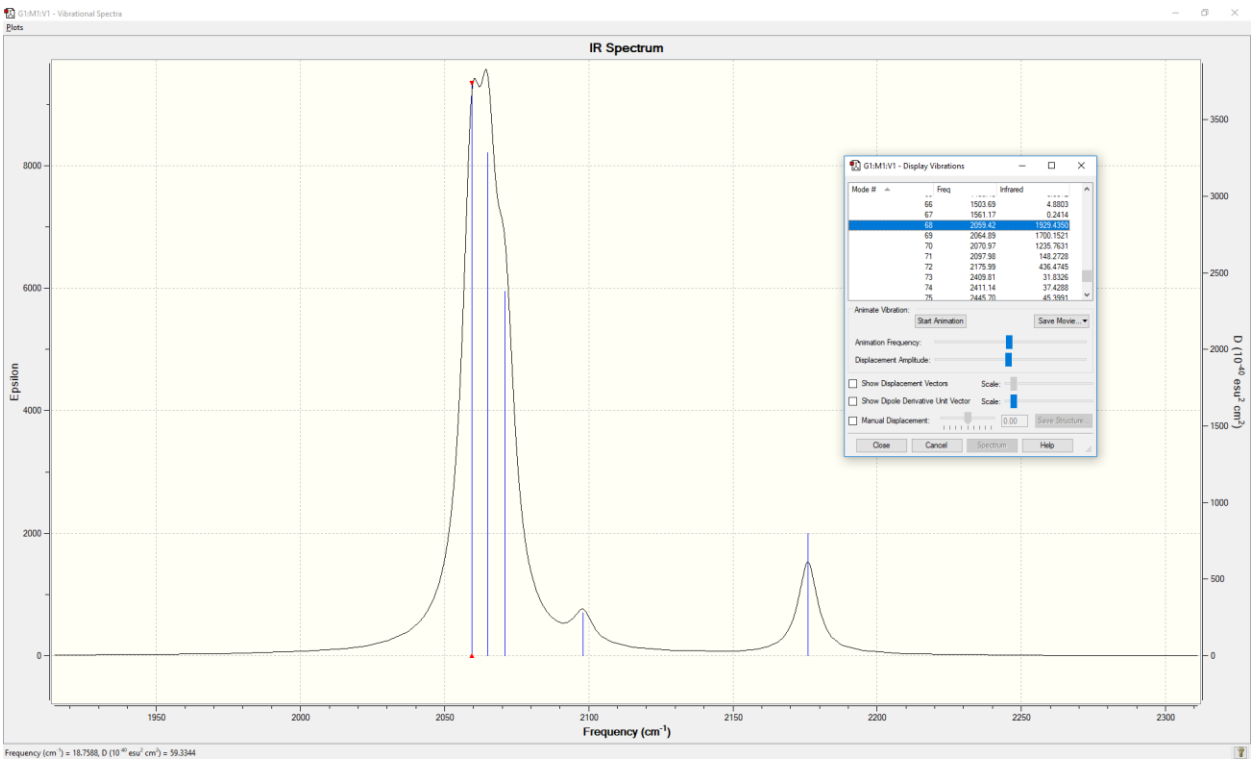


Figure 13. Optimized geometry and carbonyl region of the calculated IR spectrum for $LMo(CO)_5$.

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ptimization, frequency test and NBO6 analysis for SPHOSMo(CO)5\\0,1\P,

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Thermal correction to Gibbs Free Energy= 0.113464

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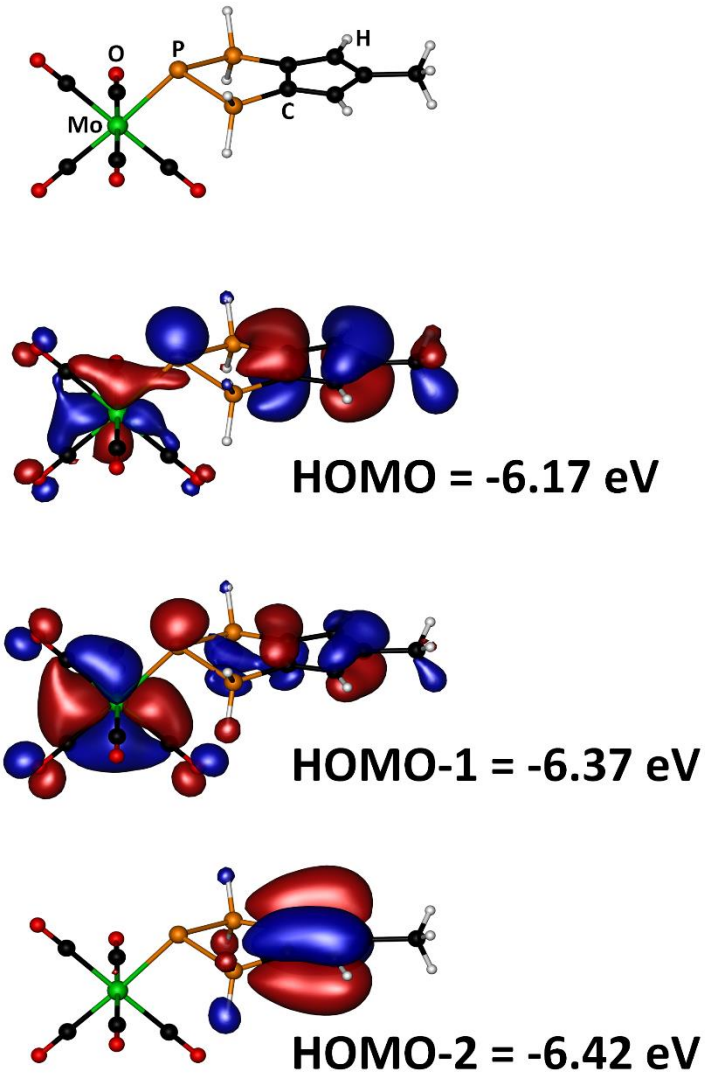
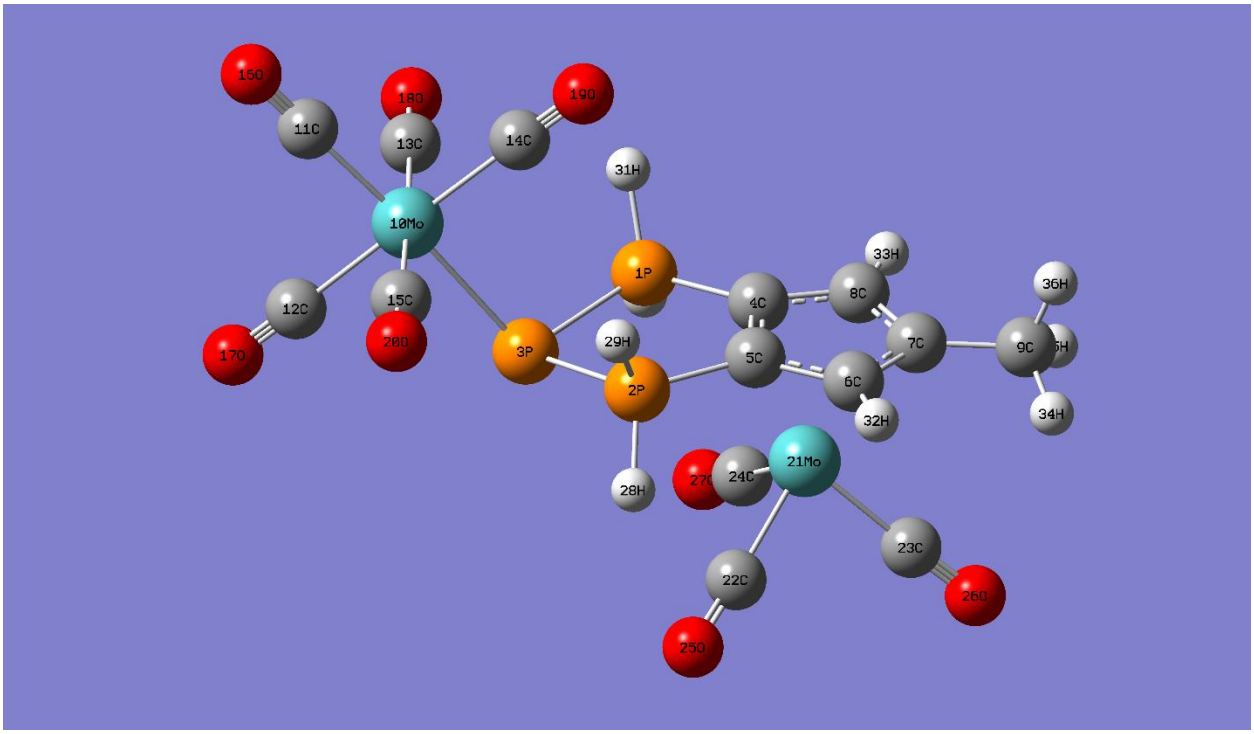


Figure 14. Frontier orbital depictions and energies for $LMo(CO)_5$.

$LMo_2(CO)_8$



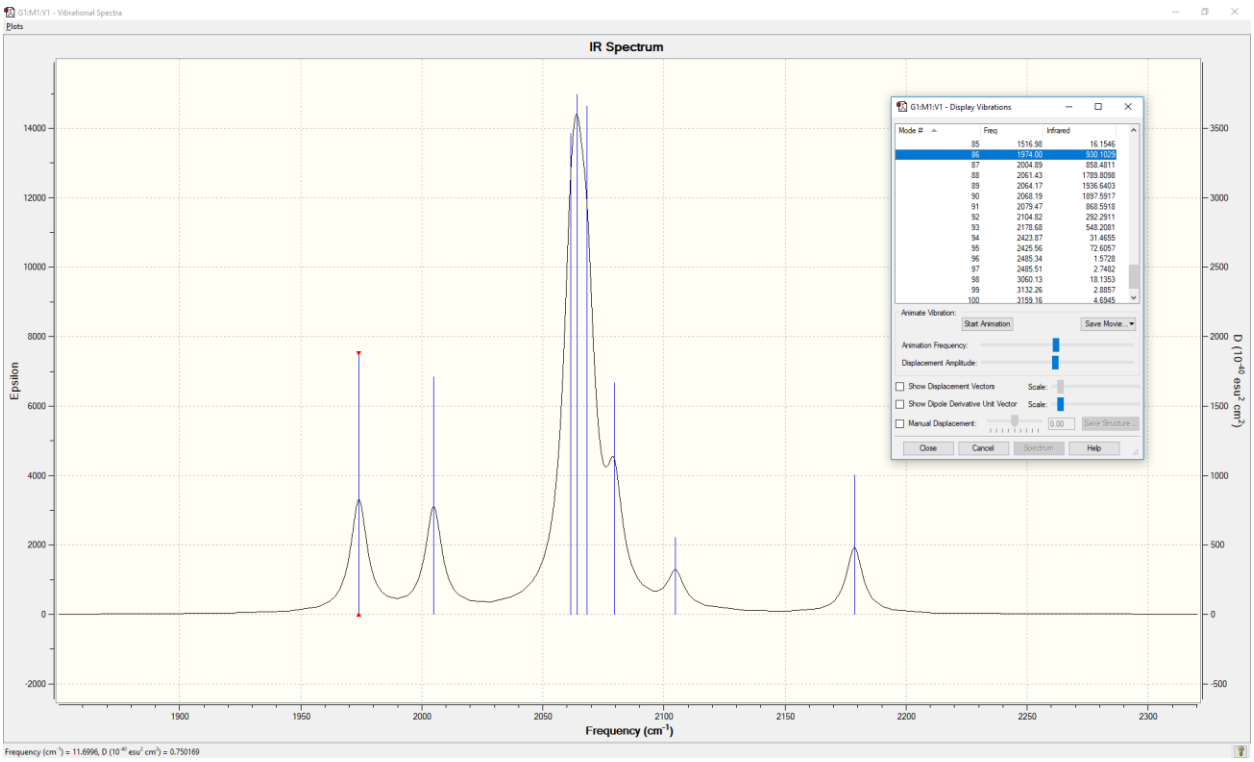


Figure 15. Optimized geometry and carbonyl region of the calculated IR spectrum for $LMo_2(CO)_8$.

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\Optimization, frequency test and NBO6 analysis for SPHOSMo2(CO)8\\0,1

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Thermal correction to Gibbs Free Energy= 0.131938

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Sum of electronic and thermal Energies= -2299.846304

Sum of electronic and thermal Enthalpies= -2299.845360

Sum of electronic and thermal Free Energies= -2299.946551

LW(CO)$_5$

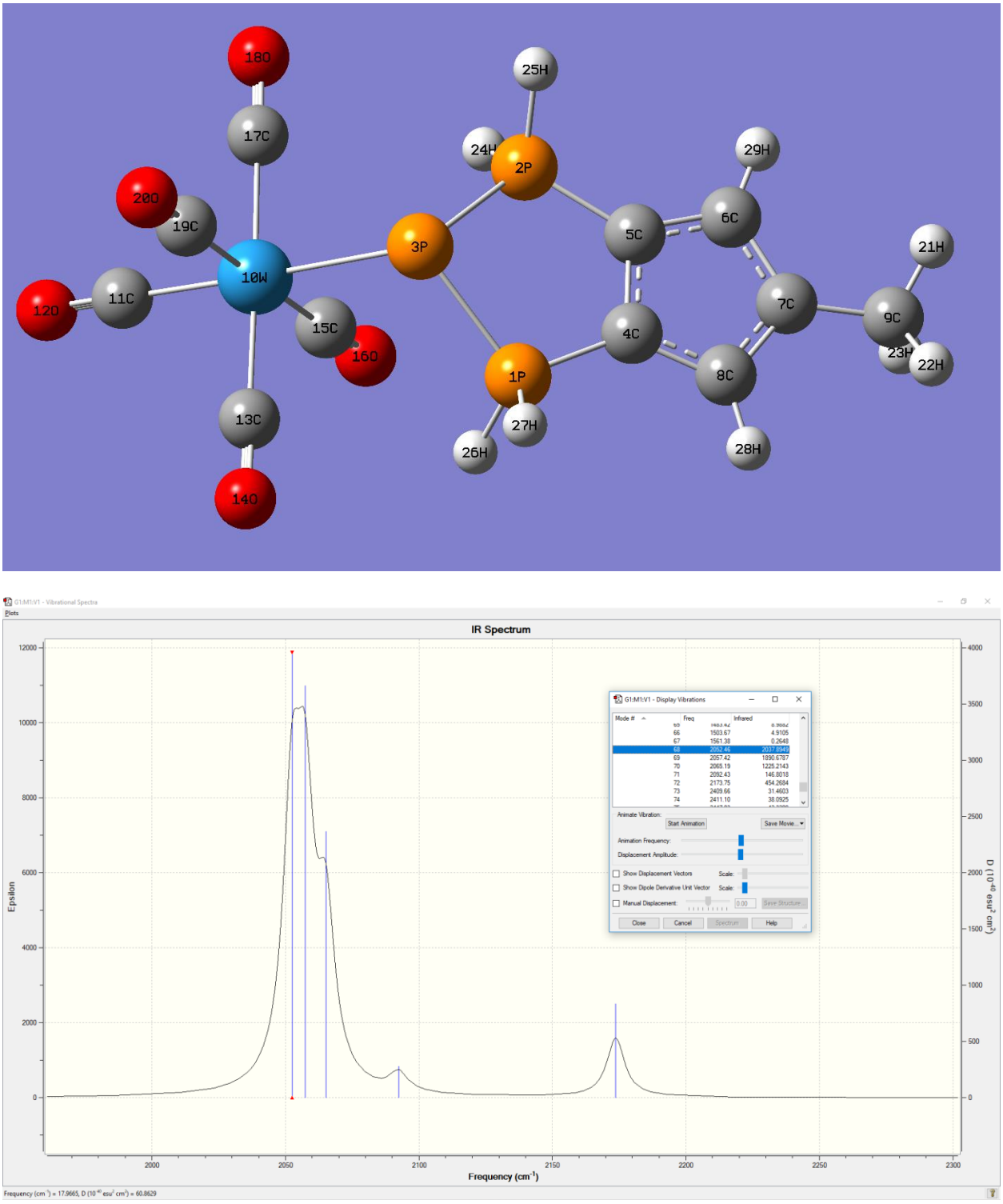

Figure 16. Optimized geometry and carbonyl region of the calculated IR spectrum for LW(CO)$_5$.

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06525,5.9577316855,8.9562227388\C,7.2208049642,4.4136115055,11.1068037

087\O,7.9739374227,3.6567417367,10.6937601996\C,6.7465458152,5.6519312

702,13.6953791626\O,7.2391242955,5.5897030272,14.7238299712\H,-0.48949

29511,-0.2968380099,9.240063619\H,-1.645238205,0.8181852242,9.97033339

07\H,-0.9615033798,1.1699803901,8.3847420007\H,4.9341966454,2.66675618

6,9.8722748266\H,4.8452705499,1.1864384345,11.4809239636\H,2.100889060

1,5.640527459,11.4083610736\H,1.5173259769,4.6791047974,13.2852413129\

H,-0.6496675746,3.1940626379,10.9961309246\H,2.1469388887,0.2546949637

,9.4799281371\\Version=EM64L-G09RevE.01\State=1-A\HF=-1890.9358606\RMS

D=3.729e-09\RMSF=1.009e-05\Dipole=-1.2481469,-1.1973227,0.0275173\Quad

rupole=0.5882865,1.4083661,-1.9966526,-7.0575175,-3.213366,2.9646218\P

G=C01 [X(C11H9O5P3W1)]\\@

Zero-point correction= 0.172076 (Hartree/Particle)

Thermal correction to Energy= 0.196190

Thermal correction to Enthalpy= 0.197134

Thermal correction to Gibbs Free Energy= 0.112538

Sum of electronic and zero-point Energies= -1890.763784

Sum of electronic and thermal Energies= -1890.739671

Sum of electronic and thermal Enthalpies= -1890.738726

Sum of electronic and thermal Free Energies= -1890.823322

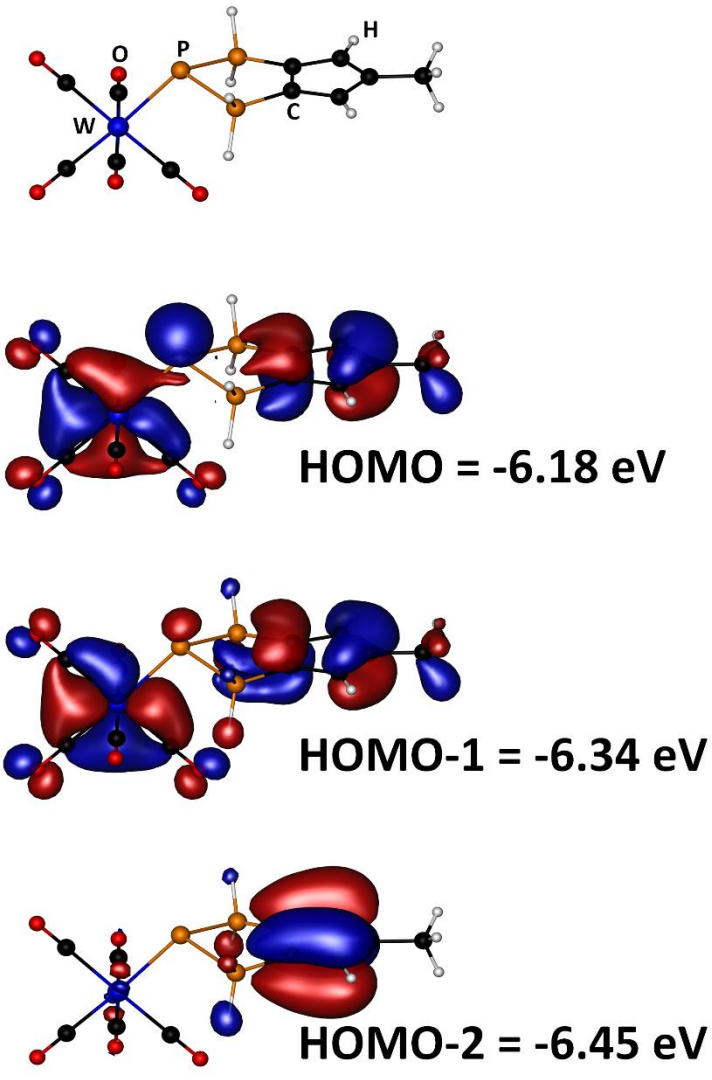

Figure 17. Frontier orbital depictions and energies for $LW(CO)_5$.

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