Supporting Information for “Transformations of Group VII Carbonyl Complexes: Possible Intermediates in a Homogeneous Syngas Conversion Scheme”

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Contents

Thermal ellipsoid plot of Re(PPh$_3$)$_2$(CO)$_3$(CHOMe) (3b)………………………………………………S2
Selected bond distances and angles for Re(PPh$_3$)$_2$(CO)$_3$(CHOMe) (3b)…………………………S2
Thermal ellipsoid plot of Mn(PPh$_3$)$_2$(CO)$_3$(CH$_2$OMe) (5a)……………………………………..S3
Selected bond distances and angles for Mn(PPh$_3$)$_2$(CO)$_3$(CH$_2$OMe) (5a)…………………………..S3
Structural parameters for 3b and 5a………………………………………………………………………………..S4
Thermal ellipsoid plot of Re(PPh$_3$)$_2$(CO)$_3$(CHOMe) (3b).

Selected bond distances and angles for Re(PPh$_3$)$_2$(CO)$_3$(CHOMe) (3b).

Re-C(1) 1.981(3)
Re-C(3) 1.993(2)
Re-C(2) 2.003(3)
Re-C(4) 2.064(3)
Re-P(1) 2.4387(4)
Re-P(1)#1 2.4388(4)
O(1)-C(1) 1.144(4)
O(2)-C(2) 1.148(3)
O(3)-C(3) 1.129(3)
O(4)-C(4) 1.290(4)
O(4)-C(5) 1.459(4)
C(4)-O(4)-C(5) 120.4(3)
O(4)-C(4)-Re 123.8(2)
Thermal ellipsoid plot of Mn(PPh$_3$)$_2$(CO)$_3$(CH$_2$OMe) (5a).

Selected bond distances and angles for Mn(PPh$_3$)$_2$(CO)$_3$(CH$_2$OMe) (5a).

Mn(1)-C(2) 1.794(3)
Mn(1)-C(1) 1.805(3)
Mn(1)-C(3) 1.846(3)
Mn(1)-C(4) 2.156(3)
Mn(1)-P(1) 2.2863(7)
Mn(1)-P(2) 2.2933(7)
O(1)-C(1) 1.169(3)
O(2)-C(2) 1.169(3)
O(3)-C(3) 1.145(3)
O(4)-C(5) 1.432(3)
O(4)-C(4) 1.455(3)
C(5)-O(4)-C(4) 111.2(2)
O(4)-C(4)-Mn(1) 113.35(16)
<table>
<thead>
<tr>
<th>Complex</th>
<th>3b</th>
<th>5a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>[C(<em>{31})H(</em>{34})O(<em>{4})P(</em>{2})Re](\cdot)0.5(CH(<em>{2})Cl(</em>{2}))</td>
<td>C(<em>{41})H(</em>{35})O(<em>{4})P(</em>{2})Mn</td>
</tr>
<tr>
<td>Mol wt</td>
<td>1242.96</td>
<td>708.57</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Cryst Syst</td>
<td>Orthorhombic</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>Space Group</td>
<td>Pmn2(_1)</td>
<td>R-3</td>
</tr>
<tr>
<td>a, Å</td>
<td>20.2321(5)</td>
<td>43.9520(16)</td>
</tr>
<tr>
<td>b, Å</td>
<td>8.8558(2)</td>
<td>43.9520(16)</td>
</tr>
<tr>
<td>c, Å</td>
<td>15.6377(4)</td>
<td>11.9031(13)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>Vol. Å(^3)</td>
<td>2801.83(12)</td>
<td>19913.5(13)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.473 Mg/m(^3)</td>
<td>1.064 Mg/m(^3)</td>
</tr>
<tr>
<td>µ, mm(^{-1})</td>
<td>2.370</td>
<td>0.403</td>
</tr>
<tr>
<td>F(000)</td>
<td>1256</td>
<td>6624</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.30 x 0.08 mm(^3)</td>
<td>0.41 x 0.08 x 0.03 mm(^3)</td>
</tr>
<tr>
<td>θ range</td>
<td>1.65 to 40.56°</td>
<td>1.79 to 27.20°</td>
</tr>
<tr>
<td>-36≤h≤36</td>
<td>49≤h≤56</td>
<td></td>
</tr>
<tr>
<td>-15≤k≤15</td>
<td>-56≤k≤32</td>
<td></td>
</tr>
<tr>
<td>-28≤l≤26</td>
<td>-15≤l≤15</td>
<td></td>
</tr>
<tr>
<td>Refractions Collected</td>
<td>74440</td>
<td>46126</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>16931</td>
<td>9850</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>16931/1/371</td>
<td>9850/0/434</td>
</tr>
<tr>
<td>Goodness-of-fit on F(^2)</td>
<td>1.016</td>
<td>1.519</td>
</tr>
<tr>
<td>Final R indices[I&gt;2sigma(I)]</td>
<td>R1 = 0.0316</td>
<td>R1 = 0.0419</td>
</tr>
<tr>
<td>wR2 = 0.0606</td>
<td>wR2 = 0.0766</td>
<td></td>
</tr>
<tr>
<td>R1 = 0.0404</td>
<td>R1 = 0.0713</td>
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</tr>
<tr>
<td>wR2 = 0.0637</td>
<td>wR2 = 0.0783</td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.141 and -1.452 e Å(^{-3})</td>
<td>0.457 and -0.285 e Å(^{-3})</td>
</tr>
</tbody>
</table>