Consider the following set of data in terms of the stretching frequency of the C≡O ligand (where dien is the tridentate ligand, NH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$).

<table>
<thead>
<tr>
<th>Complex or compound</th>
<th>$v_{\text{C≡O}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2143</td>
</tr>
<tr>
<td>[V(CO)$_6$]$^-$</td>
<td>1860</td>
</tr>
<tr>
<td>[Cr(CO)$_6$]$^0$</td>
<td>$\sim$2000</td>
</tr>
<tr>
<td>[Mn(CO)$_6$]$^+$</td>
<td>2090</td>
</tr>
<tr>
<td>[Cr(dien)(CO)$_3$]$^0$</td>
<td>1900 and 1760</td>
</tr>
<tr>
<td>[Mn(dien)(CO)$_3$]$^+$</td>
<td>$\sim$2020 and $\sim$1900</td>
</tr>
</tbody>
</table>

(i) With the aid of diagrams, describe the general bonding of a CO ligand to a metal.

The HOMO of CO is the 2p$\sigma$ orbital which is polarized towards C. CO uses this orbital to $\sigma$-donate. It is a poor $\sigma$-donor (poor base) to non-transition metal cations (including H$^+$) and to transition metals with a d$^{10}$ configuration. The $\sigma$-donation is into an empty metal orbital of the correct orientation (such as d$_z^2$ and d$_{x^2-y^2}$ in an octahedral complex):

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OC: $\rightarrow$ M $\sigma$-donation
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The LUMOs of CO are the pair of 2p$\pi^*$ orbitals. These are again polarized towards C. CO uses these orbitals to $\pi$-accept electron density from a suitable orientated d-orbital on a transition metal (such as d$_{xz}$, d$_{yz}$ and d$_{xy}$ in an octahedron. This mode of bonding involves M $\rightarrow$ CO donation or $\pi$-back donation. It requires the presence of d-electrons on the metal and good overlap between the metal and CO orbitals. The latter occurs only if the metal is in a low ($\leq$ +2) oxidation. Higher oxidation states lead to the d-orbitals being too contracted for overlap to be efficient. As the donation is into the $\pi^*$ orbitals on CO, it reduces the strength of the C≡O bond. This lengthens the C≡O bond and reduces its stretching frequency. In principle, the $\pi$-back donation could decrease the CO bond order to two or less$^*$.

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M $\rightarrow$ CO $\pi$-back donation into the two $\pi^*$ orbitals on CO
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$^*$ This weakening of the internal bonding of the ligand makes it more reactive: this is a common theme in complexes involving $\pi$-acceptor ligands and a strong reason for interest in this part of inorganic chemistry.
In the absence of each other, both these modes of bonding are fairly weak interactions as CO is intrinsically a poor σ-donor and poor π-acceptor. However, in both modes operate, they synergically enhance each other: the σ-donation leads to a build up of electron density on the (electropositive) metal. The π-back donation acts to decrease this electron density so any σ-donation enhances the π-bonding. The π-back bonding leads to an increase in electron density on the (electropositive) carbon atom which in turn enhances its ability to σ-donate.

The result is a strong M-C bond with significant σ and π-components. As the π-back donation weakens the C≡O bond, the final electron distribution is a thermodynamic compromise between strengthening the M-C at the expense of the C≡O bond.

(ii) In terms of the bonding, give a brief explanation for each of the following:

- the reduction in the wavenumber of the νC≡O bands of the coordinated ligands compared to the CO molecule;

As described above, the νC≡O stretching frequency (α wavenumber) reflects the degree of π-back bonding. The greater the amount of π-back donation, the lower νC≡O is. As the π-back donation is into the π* orbitals on CO, it weakens the CO bond and lowers its stretching frequency. All of the complexes have νC≡O stretching frequencies which are lower than for free CO indicating that π-back donation is occurring in them all.

- the variations in the wavenumber of the νC≡O bands with metal oxidation state, and

π-back donation requires good overlap between the metal d-orbitals and the ligand π* orbitals. Higher oxidation states on the metal lead to less π-back donation and hence higher νC≡O stretching frequencies. Low (or negative) oxidation states on the metal lead to greater π-back donation and hence lower νC≡O stretching frequencies. Thus, the stretching frequencies are in the order:

\[ [\text{V(CO)}_6]^\text{−} < [\text{Cr(CO)}_6]^0 < [\text{Mn(CO)}_6]^\text{+} \]
\[ [\text{Cr(dien)(CO)}_3]^0 < [\text{Mn(dien)(CO)}_3]^\text{+} \]

- the variations in the wavenumber of the νC≡O bands with the number of CO ligands.

Dien is a good σ-donor. It is not able to π-accept (or π-donate). Substitution of 3CO ligands by one dien molecule therefore leads a build up of electron density on the metal. It reduces this by increasing its π-back donation to the three remaining CO ligands. This extra π-back donation further lowers the νC≡O stretching frequencies. Thus, the stretching frequencies are in the order:

\[ [\text{V(CO)}_6]^\text{−} < [\text{Cr(CO)}_6]^0 < [\text{Mn(CO)}_6]^\text{+} \]
\[ [\text{Cr(dien)(CO)}_3]^0 < [\text{Cr(CO)}_6]^0 \]
\[ [\text{Mn(CO)}_6]^\text{+} < [\text{Mn(dien)(CO)}_3]^\text{+} \]