Supporting Information:

Hetero-dinuclear complex of 3d metals with bridging dinitrogen ligand:
Theoretical prediction of characteristic features of geometry and spin multiplicity

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Figure S1. Unexpected orbitals obtained by CASSCF calculation with twelve active orbitals. Occupation number of the $b_2$ orbital is smaller than 0.01 and that of the $a_1$ orbital is larger than 1.99.

Figure S2. Relative stabilities of various spin states in ($\mu$-$N_2$)[$M^1$(AIP)][$M^2$(AIP)].
Table S1. Important geometrical parameters (Å) of ($\mu$-$\text{N}_2$)[M$_1$(AIP)][M$_2$(AIP)] calculated by the CASSCF method.

| [M$_1$, M$_2$] | state | $\eta^2$-side-on | | state | $\eta^1$-end-on | |
|----------------|-------|------------------|---|------------------|---|
|                 |       | r(M$_1$-M$_2$)   | r(M$_1$-N) | r(M$_2$-N) | r(N-N) |       | r(M$_1$-M$_2$) | r(M$_1$-N) | r(M$_2$-N) | r(N-N) |
| [V, Cr]        | $^2$B$_2$ | 3.973 | 2.105 | 2.057 | 1.239 | | $^2$B$_2$ | 5.057 | 2.005 | 1.868 | 1.185 |
| [Cr, Mn]       | $^{10}$B$_1$ | 4.010 | 2.031 | 2.141 | 1.243 | | $^{10}$B$_1$ | 5.034 | 1.864 | 1.988 | 1.182 |
|                 | $^2$A$_2$ | 3.983 | 2.167 | 2.041 | 1.270 | | $^8$B$_2$ | 5.020 | 1.928 | 1.891 | 1.202 |
| [Mn, Fe]       | $^8$B$_2$ | 3.909 | 2.097 | 2.015 | 1.276 | | $^8$A$_2$ | 4.946 | 1.915 | 1.833 | 1.198 |
| [Cr, Fe]       | $^9$B$_1$ | 3.950 | 2.040 | 2.101 | 1.242 | | $^9$B$_1$ | 4.968 | 1.861 | 1.920 | 1.186 |
|                 | $^3$A$_2$ | 3.933 | 2.150 | 1.984 | 1.268 | | $^7$B$_2$ | 4.964 | 1.942 | 1.824 | 1.198 |
| [Cr, Co]       | $^8$B$_1$ | 3.929 | 2.041 | 2.079 | 1.242 | | $^8$B$_1$ | 4.963 | 1.865 | 1.915 | 1.183 |
|                 | $^4$A$_2$ | 3.867 | 2.152 | 1.915 | 1.260 | | $^6$B$_2$ | 4.919 | 1.958 | 1.768 | 1.193 |
| [V, V]         | $^1$A$_1$ | 3.967 | 2.079 | 2.079 | 1.250 | | $^1$A$_1$ | 5.089 | 1.947 | 1.947 | 1.196 |
| [Cr, Cr]       | $^1$A$_1$ | 3.952 | 2.070 | 2.070 | 1.232 | | $^1$A$_1$ | 5.034 | 1.881 | 1.881 | 1.180 |
| [Mn, Mn]       | $^9$B$_2$ | 3.958 | 2.080 | 2.080 | 1.278 | | $^9$A$_2$ | 5.002 | 1.900 | 1.900 | 1.201 |
| [Fe, Fe]       | $^7$B$_2$ | 3.859 | 2.032 | 2.032 | 1.275 | | $^7$A$_2$ | 4.891 | 1.848 | 1.848 | 1.195 |
Table S2. Occupation numbers of CASSCF-natural orbitals of (μ-N\(_2\))[M\(^1\)(AIP)][M\(^2\)(AIP)].

<table>
<thead>
<tr>
<th></th>
<th>[Cr, Mn]</th>
<th></th>
<th>[Cr, Fe](^a)</th>
<th></th>
<th>[Cr, Co](^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\eta^2)-side</td>
<td>(\eta^1)-end</td>
<td>(\eta^2)-side</td>
<td>(\eta^1)-end</td>
<td>(\eta^2)-side</td>
</tr>
<tr>
<td></td>
<td>(^{10})B(_1)</td>
<td>(^2)A(_2)</td>
<td>(^{10})B(_1)</td>
<td>(^8)B(_2)</td>
<td>(^9)B(_1)</td>
</tr>
<tr>
<td>(\varphi_{12})</td>
<td>0.01</td>
<td>0.00</td>
<td>0.09</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>(\varphi_{11})</td>
<td>0.04</td>
<td>0.50</td>
<td>0.20</td>
<td>0.55</td>
<td>0.04</td>
</tr>
<tr>
<td>(\varphi_{10})</td>
<td>1.00</td>
<td>0.76</td>
<td>0.92</td>
<td>0.62</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{9})</td>
<td>1.00</td>
<td>0.96</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{8})</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{7})</td>
<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td>(\varphi_{6})</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{5})</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{4})</td>
<td>1.00</td>
<td>1.04</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{3})</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>(\varphi_{2})</td>
<td>1.00</td>
<td>1.24</td>
<td>1.00</td>
<td>1.37</td>
<td>(2.00)</td>
</tr>
<tr>
<td>(\varphi_{1})</td>
<td>1.96</td>
<td>1.50</td>
<td>1.80</td>
<td>1.46</td>
<td>1.96</td>
</tr>
</tbody>
</table>

\(^a\) Parentheses are doubly occupied core orbital in the CASSCF calculation.
Table S3. Spin population at high spin state and spin-spin coupling constant J between two metal atoms.

<table>
<thead>
<tr>
<th>[M¹, M²]</th>
<th>Electronic state</th>
<th>Spin multiplicity in ground state</th>
<th>Spin population</th>
<th>J (kcal/mol)</th>
<th>RMS error (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[V, Cr]</td>
<td>B₂</td>
<td>2</td>
<td>M¹  3.00</td>
<td>M²  3.95</td>
<td>N₂  0.05</td>
</tr>
<tr>
<td></td>
<td>B₁</td>
<td>10</td>
<td>M¹  4.00</td>
<td>M²  4.97</td>
<td>N₂  0.03</td>
</tr>
<tr>
<td>[Cr, Mn]</td>
<td>A₂</td>
<td>2</td>
<td>M¹  3.95</td>
<td>M²  3.88</td>
<td>N₂  −0.84</td>
</tr>
<tr>
<td>[Mn, Fe]</td>
<td>B₂</td>
<td>8</td>
<td>M¹  4.79</td>
<td>M²  3.51</td>
<td>N₂  −1.29</td>
</tr>
<tr>
<td></td>
<td>B₁</td>
<td>9</td>
<td>M¹  4.00</td>
<td>M²  3.97</td>
<td>N₂  0.03</td>
</tr>
<tr>
<td>[Cr, Fe]</td>
<td>A₂</td>
<td>3</td>
<td>M¹  3.99</td>
<td>M²  2.65</td>
<td>N₂  −0.63</td>
</tr>
<tr>
<td>[Cr, Co]</td>
<td>B₁</td>
<td>8</td>
<td>M¹  4.00</td>
<td>M²  2.97</td>
<td>N₂  0.03</td>
</tr>
<tr>
<td></td>
<td>A₂</td>
<td>4</td>
<td>M¹  3.94</td>
<td>M²  1.69</td>
<td>N₂  −0.63</td>
</tr>
</tbody>
</table>

a) There are only two possible spin states in the A₂ state of Cr-Co complex.

The negative J value provides a low spin (doublet) except for the Cr-Co complex with the A₂ state in which the ground state has a quartet state. However, a high spin state does not always correspond to a large J value except for the Mn-Fe complex with ⁸B₂ state; for instance, the highest spin ¹⁰B₁ state of the Cr-Mn complex has a small J value.
Figure S3. (A) Schematical orbital interaction diagrams and (B) natural orbitals with occupation numbers of (μ-η^2:η^2-N_2)[Cr(AIP)][Fe(AIP)] in (a) the B1 and (b) the A2 states.

a) Upper side is Cr(AIP) and lower side is Fe(AIP). b) In parenthesis is occupation number.
Figure S4. (A) Schematical orbital interaction diagrams and (B) natural orbitals with occupation numbers of \((\mu-\eta^{2}\eta^{2}-N_{2})[\text{Cr(AIP)}][\text{Co(AIP)}]\) in (a) the A\(_{2}\) and (b) the B\(_{1}\) states.

a) Upper side is Cr(AIP) and lower side is Co(AIP). b) In parenthesis is occupation
The discussion of the spin multiplicity and the spin-polarization in the A$_2$ state of the Cr-Mn, Cr-Fe, and Cr-Co complexes.

In the Cr-Fe and Cr-Co complexes, one or two non-bonding MOs become(s) doubly occupied because the number of d electrons increases as going to the Cr-Fe and Cr-Co complexes from the Cr-Mn complex. In other words, MO diagrams are similar in these three complexes but the number of doubly occupied non-bonding d orbital is different; see Figures S2 and S3 in SI. In the Cr-Fe complex, the Cr and Fe atoms have four singly occupied non-bonding d orbitals in the B$_1$ state. Thus, the B$_1$ state can have singlet to nonet spin multiplicities by combination of those MOs. In the A$_2$ state, on the other hand, the Fe atom has two singly occupied d orbitals but the Cr atom has four. As a result, the A$_2$ state can have triplet to septet spin multiplicity by the combination of these SOMOs. In the Cr-Co complex, the Co atom has three singly occupied d orbitals in the B$_1$ state and one singly occupied d orbital in the A$_2$ state. Therefore, the B$_1$ state can have doublet to octet spin multiplicities. The A$_2$ state can have quartet to sextet spin multiplicities, whereas the doublet is not very stable due to the too small exchange interaction. Hence, it is concluded that the possible spin multiplicities are smaller in the A$_2$ state than in the B$_1$ state in these complexes.
Table S4. Main electron configurations of (μ-η²:η²-N₂)[Cr(AIP)][Mn(AIP)] in A₂ state calculated by the CASCI method with the localized molecular orbitals under C²ᵥ symmetry.

<table>
<thead>
<tr>
<th>State</th>
<th>Configuration</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr(AIP)</td>
<td>Mn(AIP)</td>
</tr>
<tr>
<td></td>
<td>dₓ², dᵧ², dₓz, dᵧz</td>
<td>dₓ², dᵧ², dₓz, dᵧz</td>
</tr>
<tr>
<td>y²</td>
<td>a a a a 0 a a a a a β β</td>
<td>a a a a a β a a a 0 a β</td>
</tr>
<tr>
<td></td>
<td>α a a a 0 a a a a a β α β</td>
<td>a a a a a β a a a a a β</td>
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<tr>
<td></td>
<td>a a a a α β a a a a a α 0 β</td>
<td>a a a a α β a a a a a α 0 a β</td>
</tr>
</tbody>
</table>

The large negative spin population indicates that spin polarization largely occurs in the A₂ state. The φ₁₁ consists of largely anti-bonding overlap between the N₂ π⁺ₓ and Mn dᵧz but moderately bonding overlap between the Cr dₓz and N₂ π⁺ₓ orbitals. Thus, the one-electron excitation from the φ₁ to the φ₁₁ moderately increases α-spin population on the Cr but considerably increases α-spin one on the Mn; see Figure 6(d) and Table S3 for the comparison with main configuration by the CASCI method for the octet and the doublet spin multiplicities in the A₂ state. However, the φ₀ is empty and the singly occupied φ₉ is perpendicular to the φ₁ and φ₁₁ MOs, leading to the moderate exchange interaction. Hence, the high spin state cannot be stabilized well and the low spin doublet state becomes the ground state. The spin distribution and the electronic state of the A₂ state...
state of the Cr-Co complex are essentially the same as those of the Cr-Mn complex.

(a)

Figure S5. (a) Active orbitals and (b) schematical picture of molecular orbitals which consist of metal \( d_{xz} \), \( d_{yz} \) and \( N_2 \, \pi^* \) orbitals in the \( ^8B_1 \) state of \( (\mu-\eta^1;\eta^1-N_2)[Cr(AIP)][Mn(AIP)] \). Upper side is Cr(AIP) and lower side is Mn(AIP). Numbers in parentheses represent occupation numbers in the ground spin state.
Difference between $A_2$ of $\eta^2$-side-on structure and $B_2$ of $\eta^1$-end-on structure in spin distribution.

In the $B_2$ state of the $\eta^2$-end-on structure, the bonding $\phi_1$ and anti-bonding $\phi_{11}$ MOs consist of the $N_2 \pi_x^*$, Mn $d_{x,z}$, and Cr $d_{x,z}$ orbitals unlike in the $A_2$ state; see Figure 7. In other words, the 3-center $d_x\pi^*$ interaction is formed like in $(\mu$-$N_2)[Mn(AIP)][Fe(AIP)]$. This is consistent with the geometrical feature that the Mn-N distance is only 0.03 Å shorter than the Cr-N distance in the $B_2$ state with $\eta^1$-end-on structure, while that is 0.1 Å shorter in the $A_2$ state with $\eta^2$-side-on, as shown in Table 2. Thus, the spin polarization induced by one-electron excitation from $\phi_1$ to $\phi_{11}$ increases the $\alpha$-spin density on Cr and Mn atoms and the $\beta$-spin density on the dinitrogen moiety; see Table 3. These features are favorable for high spin state. Because the contribution of Cr $d_{yz}$ is small in the $\phi_{10}$, one-electron transfer from $\phi_2$ to $\phi_{10}$ little changes spin density on Cr. As a result, the ground state has high spin multiplicity in the $B_2$ state; see Figure S4.