# A Facile and New Type of Route to the Redox-active Rigid-rod Complex $[\{Mn(dmpe)_2(C{\equiv}CH)\}_2(\mu\text{-}C_4)][PF_6]$ via $Mn\text{-}C_2^{\cdot}$ Radical Coupling

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## Computational details

All calculations reported in the paper were performed using the Amsterdam Density Functional program package ADF, release 2000.01.[1] The Vosko-Wilk-Nusair parametrization[2a] was used for the local-density approximation (LDA) with the addition of gradient corrections due to Becke[2b] and Perdew[2c] (GGA). The hydrogen atom was represented by a double-ξ STO basis function for the 1s orbital and a single-ξ 2p polarization function (ADF database III). The frozen-core approximation was applied for the 1s electrons of the carbon atom, and for the 1s, 2s and 2p electrons of phosphorus and manganese elements. The valence shells of these non-hydrogen elements were described with a triple-ξ STO basis set plus one polarization function (ADF database IV). Optimized geometries and bonding energies of the singlet and triplet states of the model complex $Mn(dHpe)_2(C{\equiv}CH)(C{\equiv}C)$ are given below.

## References

1 (a) E. J. Baerends, D. E. Ellis, and P. Ros Chem. Phys. 1973, **2**, 41; (b) L. Versluis and T. Ziegler J. Chem. Phys. 1988, **322**, 88; (c) G. te Velde and E. J. Baerends J. Comput. Phys. 1992, **99**, 84; (d) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends Theor. Chem. Acc. 1988, **99**, 391.

2 (a) S.H. Vosko, L. Wilk and M. Nusair Can. J. Phys. 1980, **58**, 1200; (b) A.D. Becke Phys. Rev. A 1988, **38**, 3098; (c) J.P. Perdew Phys. Rev. B 1986, **33**, 8822.

## Optimized geometries and bonding energies

**$(dHpe)_2Mn(C{\equiv}C)(C{\equiv}CH)$ spin 0**

```
ADF 2000.01  RunTime: Dec12-2000 09:26:33

GEOMETRY OPTIMIZATION

Final Geometry   (x,y,z in Angstrom)

Mn     0.000000    0.000000    0.082648
P      2.253147    0.022778   -0.000721
P     -0.166086    2.247627    0.091929
C      0.000000    0.000000   -1.773127
C      0.000000    0.000000    2.042846
P      0.166086   -2.247627    0.091929
P     -2.253147   -0.022778   -0.000721
C      0.000000    0.000000    3.282060
H      0.000000    0.000000    4.355714
C      0.000000    0.000000   -3.078194
C      2.847108   -1.679833   -0.560787
H      2.991706    0.870171   -0.888507
H      3.038908    0.223449    1.184376
C     -1.992764    2.758332    0.117593
H      0.332433    3.003219   -1.018994
H      0.341359    3.069364    1.151973
C      1.992764   -2.758332    0.117593
H     -0.332433   -3.003219   -1.018994
H     -0.341359   -3.069364    1.151973
C     -2.847108    1.679833   -0.560787
H     -2.991706   -0.870171   -0.888507
H     -3.038908   -0.223449    1.184376
H      2.705691   -1.693511   -1.651980
H      3.917156   -1.811314   -0.346359
H      2.262330   -2.853935    1.180418
H      2.123153   -3.741389   -0.355827
H     -2.262330    2.853935    1.180418
H     -2.123153    3.741389   -0.355827
H     -2.705691    1.693511   -1.651980
H     -3.917156    1.811314   -0.346359

Total  Bonding  Energy:
-5.637425841973375 hartree
-3537.54       kcal/mol
-14801.06        kJ/mol

Total Charge:         0.00
Spin Polarization:    0.00

Summary Geometry Optimization
       Item          Value      Criterion
-----------------------------------------
change in energy  -0.00001868   0.00300000
gradient max       0.00262557   0.00300000
gradient rms       0.00056906   0.00333333
=========================================
```

**$(dHpe)_2Mn(C{\equiv}C)(C{\equiv}CH)$ spin 2**

```
ADF 2000.01  RunTime: Jan09-2001 14:58:33

GEOMETRY OPTIMIZATION

Final Geometry   (x,y,z in Angstrom)

Mn     0.000000    0.000000    0.086868
P      2.261707   -0.007789    0.012469
P     -0.195360    2.256896    0.076283
C      0.000000    0.000000   -1.771384
C      0.000000    0.000000    2.074268
P      0.195360   -2.256896    0.076283
P     -2.261707    0.007789    0.012469
C      0.000000    0.000000    3.308526
H      0.000000    0.000000    4.382106
C      0.000000    0.000000   -3.069486
C      2.874458   -1.694785   -0.565399
H      3.006235    0.859772   -0.849505
H      3.027708    0.182483    1.211725
C     -2.015569    2.784463    0.088084
H      0.320094    2.994357   -1.036285
H      0.314308    3.083476    1.131514
C      2.015569   -2.784463    0.088084
H     -0.320094   -2.994357   -1.036285
H     -0.314308   -3.083476    1.131514
C     -2.874458    1.694785   -0.565399
H     -3.006235   -0.859772   -0.849505
H     -3.027708   -0.182483    1.211725
H      2.746136   -1.693981   -1.658009
H      3.941800   -1.820680   -0.335131
H      2.284715   -2.908550    1.147952
H      2.134491   -3.756200   -0.410477
H     -2.284715    2.908550    1.147952
H     -2.134491    3.756200   -0.410477
H     -2.746136    1.693981   -1.658009
H     -3.941800    1.820680   -0.335131

Total  Bonding  Energy:
-5.671409668487392 hartree
-3558.86       kcal/mol
-14890.29        kJ/mol

Total Charge:         0.00
Spin Polarization:    2.00
Spin Density:
#  Atom   Spin
--------------------
1  Mn     1.4533
10  C     0.6098

Summary Geometry Optimization
       Item           Value      Criterion
-------------------------------------------
change in energy    -0.00003351   0.00300000
gradient max         0.00118426   0.00300000
gradient rms         0.00039765   0.00333333
===========================================
```