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$Dcab^{2-}$-Substituted Manganese Vinylidene Complexes as Better Electron Reservoirs: A DFT Study

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Mononuclear vinylidene complexes of the type $Mn(C_5H_4R')(R''_2PCH_2CH_2P\ R''_2){=}C{=}C(R^1)(H)$ are synthesized and reported by Venkatesan et al. as potential electron reservoirs, which can store and release electrons in a reversible fashion. However, the slow oxidation of the parent compound leads to an undesired product. In our model compound $Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H)$, we substituted the cyclopentadienyl moiety by the isolobal dianionic dicarbollyl ligand $Dcab^{2-}$ ($C_2B_9H_{11}{}^{2-}$) and investigated whether this simple substitution can reduce the production of an undesired product. Our calculations of vertical electron detachment energy, thermodynamic feasibility, and molecular orbital analysis (with substituents R = H, Me, Ph on the C_β atom of our model system) show that the substitution is thermodynamically favorable and leads to easy oxidation of the parent compound, easy dimerization, and better reversibility. Our comparative study between $Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H)$ and $Mn(Dcab)(PH_3)_2{=}C{=}C(R)(H)^-$ (where R = H, Me, Ph) predicts the latter to be a better electronic reservoir.

Introduction

Molecular devices are always of great interest for the advancement of technology. Molecular electronics is one of the leading areas of science where the main interest is to design electron reservoirs and molecular wires.[1−14] Electron reservoirs can store and release electrons in a reversible fashion. Earlier people thought about organic compounds for this purpose. However, due to their inability to work at high temperature, organic compounds were replaced by organometallic systems. Floriani and co-workers[15] proposed the use of the $C{=}C$ bond for storing and releasing electrons in transition metal complexes. High-temperature stability and the possibility of tuning the HOMO−LUMO gap by changing the metal center make organometallic systems very interesting and important for the design of electron reservoirs. Electron-rich manganese-centered vinylidene complexes have been exploited by many due to their low-energy work function.[16] Manganese vinylidene complexes of the type $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2){=}C{=}C(R^1)(H)$ were designed and synthesized for application as molecular batteries.[16] Earlier reports by Terry et al.[17] indicated that vinylidene complexes of the type $Mn(C_5H_5)(CO)_2{=}C{=}C(H)_2$ were thermally unstable and thus had to be generated and studied at low temperature. Later Venkatesan et al. used bidentate phosphorus ligands $Me_2PCH_2CH_2PMe_2$ (dmpe) and $Et_2PCH_2CH_2PEt_2$ (depe) to obtain isolobal compounds that are thermally stable.[16] The complex $Mn(C_5H_4R')(R''_2PCH_2CH_2P\ R''_2){=}C{=}C(R^1)(H)$ can be oxidized to form radical cations, which can combine to form dinuclear carbyne complexes $(C_5H_4R')(R''_2PCH_2CH_2PR_2'')Mn{\equiv}CC(R^1)(H)C(R^1)(H)C{\equiv}Mn(R''_2PCH_2CH_2PR''_2)(C_5H_4R')^{2+}$ (Scheme 1). The dinuclear carbyne complex can be reduced to get back the parent compound.

Such reactions are significant in many aspects: (1) C−C bond formation and cleavage are reversible; (2) C−C bond cleavage acts as a shuttle of two electrons; (3) electron transfer can occur intermolecularly. Because of the reversible nature, these molecules can be used as molecular reservoirs. However, the too slow oxidation of the parent compound leads to the formation of an undesired product (Scheme 1). Slow oxidation of the starting vinylidene complex leaves the radical cation enough time to undergo proton transfer to the residual vinylidene complex, which can act as base and form the stable carbyne complexes.[18] The remaining $(C_5H_4R')(R''_2PCH_2CH_2PR''_2)Mn{-}C{\equiv}C{-}R^1$ complexes, being radicals as well, undergo self-coupling reaction and produce the undesired product (Scheme

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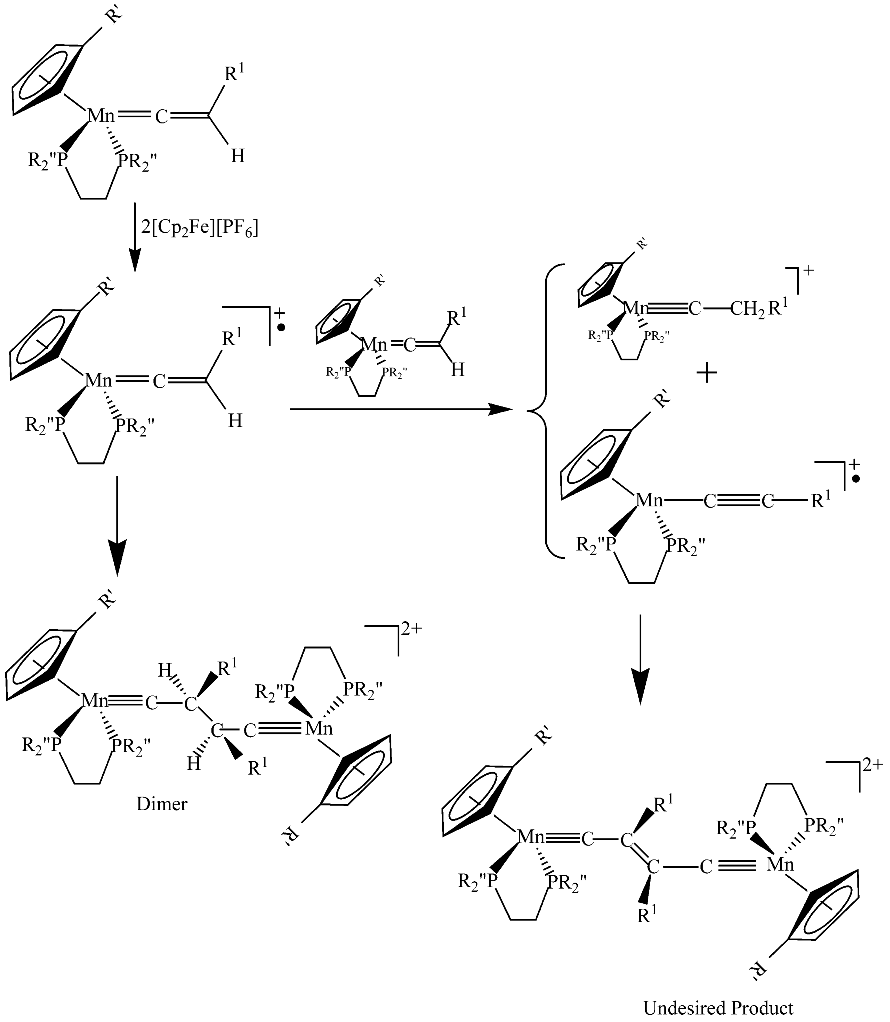
Scheme 1



1). Only a few theoretical investigations have been performed at the DFT level on the transition metal vinylidene complexes in recent years.[19−22] The effects of auxiliary phosphine ligands, the substituents on the C_β atom, and the cyclopentadienyl ligand on the redox and structural properties have been extensively studied and reported[1,2,16] experimentally and theoretically.

In this paper, we have analyzed the possibility of terminating the undesired pathway of this reaction. Our idea is to substitute the C_p^- group with isolobal $Dcab^{2-}$ in our model compound $Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H)$ where R = H, Me, and Ph. The dicarbollyl ($Dcab^{2-}$) species is a versatile ligand that is an isolobal inorganic analogue of the Cp^- ion. The formal replacement of the mononuclear Cp^- ligand with isolobal dianionic dicarbollyl ligand $Dcab^{2-}$ will increase the overall charge by one unit, but leaves the gross structural and metal frontier orbital properties unchanged. Consequently, the energy needed for the removal of one electron should be easier (easy oxidation). So the formation of the undesired product due to slow oxidation should be reduced. The neutral radicals in the case of the $Dcab^{2-}$-substituted parent compound should undergo easy coupling to give the desired dimer. The synthesis and structures of constrained-geometry aluminum and group 4 metal complexes have been reported,[23,24] where instead of a Cp^- ligand, an isolobal $Dcab^{2-}$ ligand has been used to modify the metal−ligand interaction.

Computational Details

All the structures of our model systems are fully optimized using Gaussian03 software.[25] We used the B3LYP[26,27] method with the LANL2DZ[28] basis set. This uses Becke's well-known three-parameter functional, including Hartree−Fock exchange contributions with nonlocal correlation for exchange potential, together with

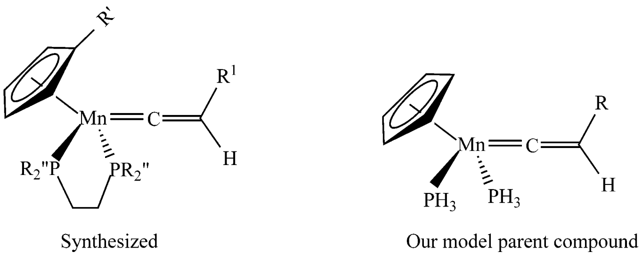


Figure 1. Synthesized and model compounds.

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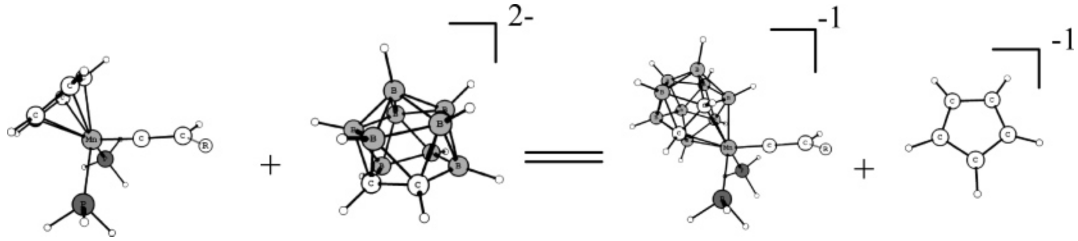

Figure 2.

Table 1. Structural Parameters for Half-Sandwich Manganese Parent Compounds. (geometrical parameters for the corresponding experimentally characterized structures are in parentheses)

	$Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H)$						$Mn(Dcab)(PH_3)_2{=}C{=}C(R)(H)^-$					
R	$Mn-C_\alpha$ (Å)	$C_\alpha-C_\beta$ (Å)	$Mn-P$ (Å)	$C_\beta-R$ (Å)	$Mn-C_\alpha-C_\beta$ (deg)	$C_\alpha-C_\beta-R$ (deg)	$Mn-C_\alpha$ (Å)	$C_\alpha-C_\beta$ (Å)	$Mn-P$ (Å)	$C_\beta-R$ (Å)	$Mn-C_\alpha-C_\beta$ (deg)	$C_\alpha-C_\beta-R$ (deg)
H	1.76	1.34	2.31	1.09	177.3	121.9	1.76	1.35	2.31	1.09	178.9	121.6
	(1.76)	(1.32)			(176.6)							
Me	1.77	1.34	2.31	1.53	176.7	125.2	1.77	1.35	2.30	1.53	176.1	125.1
Ph	1.75	1.35	2.31	1.48	176.8	127.1	1.74	1.36	2.32	1.47	178.7	126.1
	(1.74)	(1.35)	(2.20)	(1.47)	(179.5)	(127.1)						

nonlocal correlation for the correlation energy suggested by Lee, Yang, and Parr.[27] We have used the trial version of the ChemCraft[29] program for the visualization and molecular orbital analysis. For open-shell systems we performed unrestricted UB3LYP calculation. We have used toluene as a solvent in our calculations. The effect of solvent is taken into account using the polarizable continuum model.[30,31] In this method the solvent is modeled as a continuum of uniform dielectric constants. The solute is placed into a cavity within the solvent. A dipole in the molecule will induce a dipole in the medium, and the induced dipole in turn interacts with the molecular dipole for net stabilization. We have used the CPCM model, where the cavity is defined as the union of a series of interlocking atomic spheres. Single-point calculations on the optimized gas-phase geometries with the polarizable continuum model were performed on the selected model complexes to calculate thermodynamic feasibility of dimerization and molecular orbital analysis.

Frequency calculations have been done for all the structures except for $(Dcab)(PH_3)_2Mn{\equiv}C-C(Ph)(H)-C(Ph)(H)-C{\equiv}Mn(PH_3)_2(Dcab)$ because of higher computational cost. All the reported structures are true minima on the potential energy surface except $(C_5H_5)(PH_3)_2Mn{\equiv}C-C(H)(H)-C(H)(H)-C{\equiv}Mn(PH_3)_2(C_5H_5)^{2+}$. Though we observed a single negative frequency associated with this structure (-12 cm^{-1}), which corresponds to the rotation of the $(C_5H_5)(PH_3)_2Mn$ unit, the similar compound $(C_5H_4Me)(H_2PCH_2CH_2PH_2)_2Mn{\equiv}CC(H)(H)C(H)(H)C{\equiv}Mn(H_2PCH_2CH_2PH_2)_2(C_5H_4Me)^{2+}$ (where instead of two PH_3 ligands, a bidentate $H_2PCH_2CH_2PH_2$ ligand is present) has been synthesized and reported.[2]

Our Model Compound

Venkatesan et al. have synthesized and analyzed the properties of $Mn(C_5H_4R')(R''_2PCH_2CH_2PR''_2){=}C{=}C(R^1)(H)$ (Figure 1). We consider $Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H)$ (Figure 1) as our model parent compound to reduce the computational cost. Bidentate ligands are reported[16] to give high-temperature stability. Our objective is to study the relative stability and reactivity between the half-sandwich Cp$^-$- and Dcab^{2-}-substituted model compounds. The optimized structural parameters for Cp$^-$- and Dcab^{2-}-substituted model compounds are given in Table 1. The $Mn{=}C_\alpha$ and $C_\alpha{=}C_\beta$ distances support their double-bond nature (Table 1).

Table 2. Vertical Electron Detachment Energy (kcal/mol)

R[a]	Cp$^-$-capped parent compound	Dcab^{2-}-capped compound
H	132	56
Me	128	55
Ph	129	58

[a] R is C_β substituent.

Table 3. Δ*E* (kcal/mol) for Dimerization

R	scheme A Δ*E*	scheme B Δ*E*
H	5.25	−16.21
Me	12.07	−6.72
Ph	19.91	1.58

Results and Discussion

(a) Thermodynamic Feasibility of Substitution. We first analyzed the thermodynamic feasibility for the substitution of Cp$^-$ by Dcab^{2-} in our model compound using the following isodesmic equation.

$$Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H) + C_2B_9H_{11}{}^{2-} \rightarrow Mn(C_2B_9H_{11})(PH_3)_2{=}C{=}C(R)(H)^- + C_5H_5{}^-$$

The values of the energy difference (in kcal/mol) between the product and the reactant for the reaction (Figure 2) of the model compounds are −69, −74, and −73 for the β-substituent H, Me, and Ph, respectively. The high exothermicity of these reactions indicates that the substitution by Dcab^{2-} is thermodynamically favored.

(b) Vertical Electron Detachment Energy. We have calculated the vertical electron detachment energy for the Cp$^-$-substituted parent model compounds and the Dcab^{2-}-substituted model compounds. The results are given in Table 2. The lower value of vertical electron detachment energy for the Dcab^{2-}-substituted model compounds clearly indicates easy oxidation for these complexes, which in return supports the easy radical formation. Hence the undesired product formation due to very slow oxidation should be reduced to a great extent. The easy oxidation is the result of the unit negative charge present in the Dcab^{2-}-substituted model compounds.

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Table 4. Structural Parameters for the Dimers (geometrical parameters for the corresponding experimentally characterized structures are in parentheses)

	Cp-containing dimer						Dcab-containing dimer					
R	$Mn-C_\alpha$ (Å)	$C_\alpha-C_\beta$ (Å)	$C_\beta-C_\beta'$ (Å)	$Mn-C_\alpha-C_\beta$ (deg)	$C_\alpha-C_\beta-C_\beta'$ (deg)	$C_\alpha-C_\beta-R$ (deg)	$Mn-C_\alpha$ (Å)	$C_\alpha-C_\beta$ (Å)	$C_\beta-C_\beta'$ (Å)	$Mn-C_\alpha-C_\beta$ (deg)	$C_\alpha-C_\beta-C_\beta'$ (deg)	$C_\alpha-C_\beta-R$ (deg)
H	1.63	1.49	1.57	173.6	113.8	108.5	1.63	1.48	1.56	171.9	113.3	109.1
Me	1.63	1.49	1.58	173.9	112.3	110.1	1.63	1.49	1.58	174.9	111.8	109.4
Ph	1.64 (1.65)	1.49 (1.49)	1.59 (1.50)	174.2 (176.0)	111.8 (114.6)	109.7 (108.2)	1.63	1.49	1.59	177.1	112.1	111.6

(c) Thermodynamic Feasibility of Dimerization. The formation of dimer certainly depends on the recombination of radicals. Radical recombination reactions have been analyzed by the following scheme:

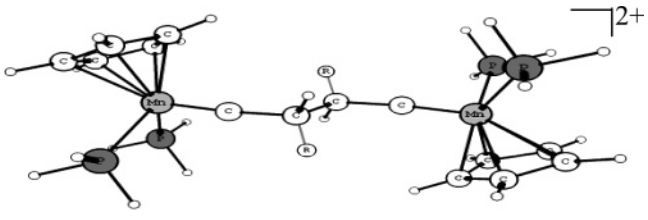
Scheme A

$$2[Mn(C_5H_5)(PH_3)_2{=}C{=}C(R)(H)]^{+\bullet} \rightarrow (C_5H_5)(PH_3)_2Mn{\equiv}C\text{-}C(R)(H){-}C(R)(H){-}C{\equiv}Mn(PH_3)_2(C_5H_5)^{2+}$$

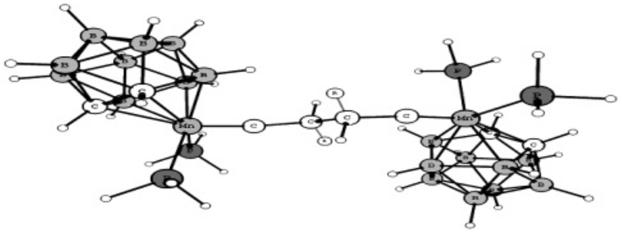
Scheme B

$$2[Mn(Dcab)(PH_3)_2{=}C{=}C(R)(H)]^{\bullet} \rightarrow (Dcab)(PH_3)_2Mn{\equiv}CC(R)(H)C(R)(H)C{\equiv}Mn(PH_3)_2(Dcab)$$

The energy difference between the product and the reactant has been calculated (Table 3). The two dimers generated from scheme A and scheme B are shown in Figure 3. The relative study shows that the dimerization process is thermodynamically favored in the case of scheme B (Table 3). There are two governing factors, steric repulsion and electrostatic effect, for this process. In scheme B the absence of electrostatic repulsion between the neutral radicals should lead to fast dimerization and formation of a stable neutral dimer. The structural parameters of the dimer species are given in Table 4. The signatures of the triple bond between Mn and C_α and the single bond between C_β and C_β' are clearly shown in Table 4. The $C_\alpha-C_\beta$ bond distances (1.48−1.49 Å) are on the short side of a C−C single bond, presumably reflecting a residual double-bond character. These structural parameters agree well with the experimentally reported structures.[16] The calculated electron affinities (in kcal/mol) of the neutral $Dcab^{2-}$-substituted dimers are −26.09, −27.48, and −28.97 for the β substituents H, Me, and Ph, respectively. The negative electron affinity indicates that the acceptance of an electron should be easy for $Dcab^{2-}$-substituted dimers.



Cp^- substituted dimer



$Dcab^{2-}$ substituted dimer

Figure 3.

Table 5. HOMO−LUMO Gap (in eV)

R	HOMO−LUMO gap Cp containing-dimer	HOMO − LUMO gap Dcab containing-dimer
H	4.53	4.24
Me	4.47	4.23
Ph	4.35	4.16

(d) Molecular Orbital Analysis and Reversibility. Oxidative coupling produces the dimer. However, for the purpose of molecular electronics the reductive decoupling of the dimer is very crucial to get back the parent compound, i.e., reversibility. The reversibility of this process could be explained if we analyze the shape of the LUMO for the dimer (see Figure 4). This unoccupied molecular orbital has π-type antibonding interaction between the Mn and C_α and σ-type antibonding interaction between $C_\beta-C_\beta'$. The addition of two electrons into this LUMO destabilizes the $Mn{\equiv}C_\alpha$ and $C_\beta-C_\beta'$ bonds, which leads to the formation of the parent compound. The energy difference between the HOMO−LUMO of the dimer represents its hardness. A small difference corresponds to soft molecules having low absolute hardness.[32] The HOMO−LUMO gaps for the model compounds are given in Table 5. The smaller HOMO−LUMO gap in the case of $Dcab^{2-}$-substituted dimers indicates easier reductive decoupling.

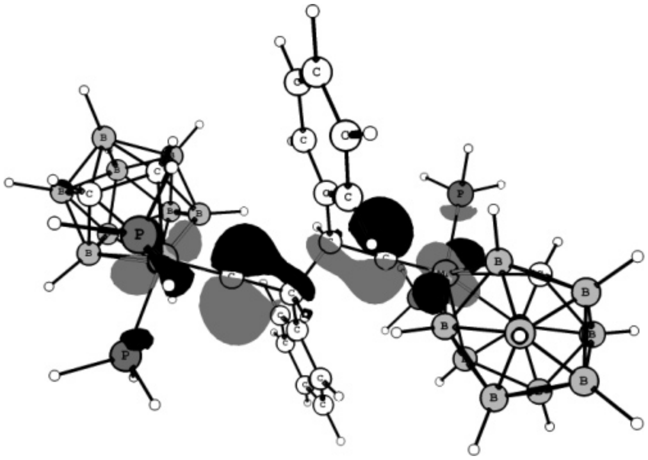


Figure 4. LUMO of our Model Dimer.

Conclusion

Our comparative study between Cp^-- and $Dcab^{2-}$-containing half-sandwich manganese complexes clearly indicates that the latter is a better candidate as an electron reservoir. Our study shows that the substitution by a $Dcab^{2-}$ ligand into the parent Cp^- half-sandwich manganese complex is thermodynamically feasible and leads to (1) lower vertical electron detachment energy (easy oxidation), (2) easy radical coupling (easy dimer-

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ization), and (3) easy reductive decoupling of the dimer (better reversibility).

We believe that our work will pave the way for the synthesis of Dcab^{2-}-substituted complexes, which could be more efficient components of molecular electronics.

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Supporting Information Available: Cartesian coordinates, total energy (in hartree), and number of imaginary frequencies for all the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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