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"Bonding in Transition Metal Silyl Dimers.
Molecular Orbital Theory"

by

Alfred B. Anderson, Paul Shiller, Eugene A. Zarate,
Claire A. Tessier-Youngs, and Wiley J. Youngs

AD-A208 269

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| REPORT DOCUMENTATION PAGE | | Form Approved OMB No. 0704-0188 |
|---|---|---|

| 1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED | | 1b. RESTRICTIVE MARKINGS |
|---|---|---|
| 2a SECURITY CLASSIFICATION AUTHORITY | | 3. DISTRIBUTION/AVAILABILITY OF REPORT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED |
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| 4 PERFORMING ORGANIZATION REPORT NUMBER(S) No. 2 | | 5. MONITORING ORGANIZATION REPORT NUMBER(S) N00014-86-K-0640 |
|---|---|---|

| 6a NAME OF PERFORMING ORGANIZATION WILEY J. YOUNGS CASE WESTERN RESERVE UNIVERSITY | 6b OFFICE SYMBOL (If applicable) | 7a. NAME OF MONITORING ORGANIZATION OFFICE OF NAVAL RESEARCH Dr. HAROLD GUARD |
|---|---|---|
| 6c. ADDRESS (City, State, and ZIP Code) DEPARTMENT OF CHEMISTRY CASE WESTERN RESERVE UNIVERSITY CLEVELAND, OHIO 44106 | | 7b. ADDRESS (City, State, and ZIP Code) CODE 1113 800 N. QUINCY STREET ARLINGTON, VA 22217 |

| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR | 8b. OFFICE SYMBOL (If applicable) | 9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER |
|---|---|---|

| 8c. ADDRESS (City, State, and ZIP Code) (see 7b) | 10 SOURCE OF FUNDING NUMBERS |
|---|---|

| PROGRAM ELEMENT NO | PROJECT NO | TASK NO. | WORK UNIT ACCESSION NO. |
|---|---|---|---|
| | | | |

11 TITLE (Include Security Classification)
"Bonding in Transition Metal Silyl Dimers. Molecular Orbital Theory"

12 PERSONAL AUTHOR(S)
Alfred B. Anderson, Paul Shiller, Eugene A. Zarate, Claire A. Tessier-Youngs and Wiley J. Youngs

| 13a TYPE OF REPORT TECHNICAL | 13b TIME COVERED FROM _____ TO _____ | 14 DATE OF REPORT (Year, Month, Day) May 5, 1989 | 15 PAGE COUNT |
|---|---|---|---|

16 SUPPLEMENTARY NOTATION
Accepted for Publication in Organometallics

| 17 COSATI CODES | | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) |
|---|---|---|---|
| FIELD | GROUP | SUB-GROUP | |
| | | | |
| | | | |

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

SEE ATTACHED

| 20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS | 21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED |
|---|---|
| 22a NAME OF RESPONSIBLE INDIVIDUAL | 22b TELEPHONE (Include Area Code) | 22c OFFICE SYMBOL |

DD Form 1473, JUN 86          Previous editions are obsolete          SECURITY CLASSIFICATION OF THIS PAGE

Bonding in Transition Metal Silyl Dimers.

Molecular Orbital Theory

by

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Eugene A. Zarate, Claire A. Tessier-Youngs, and Wiley J. Youngs

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## Abstract

Molecular orbital studies of $Mn_2(CO)_8(Si(C_6H_5)_2)_2$ and $Pt_2(H_3P)_4(SiC_6H_5Cl)_2$ have been made by interacting disilene fragments with transition metal dimers. In the former complex, it is found that the Mn-Mn distance is close to the sum of the atomic radii because the Mn-Mn bond order is 1. This leads to a long Si-Si distance and allows strong Si-Mn bond formation. In the latter complex, the Pt-Pt bond order is 0, so the disilene, with Si-Si bond intact, binds to the Pt atoms by means of ordinary $\pi$ donation and back-donation to $\pi^*$. Based on these findings, the M-M and Si-Si distances in other known transition metal-silyl four-membered rings are discussed.

The applications of polysilanes[1] have produced considerable interest in their synthesis by transition metal catalysis.[2-4] Attempts to isolate compounds from such catalytic mixtures have led to the isolation of bimetallic ($M_2Si$) or dimeric ($(MSi)_2$ transition metal silyl complexes.[3,4] Several different types of structures have been found for metal-silyl dimers[3-12] but no attempt has been made to describe the bonding in these species. To address this need and to begin to understand structure/bonding/catalytic activity relationships we have undertaken a theoretical study of two types of dimeric metal-silyl complexes.

With the exception of $Ti_2(C_5H_5)_4H_2(Si(C_6H_5)H)_2$,[4a] and the recently synthesized series $[((C_2H_5)_3P)_2Pt(Si(C_6H_5)X)(Si(C_6H_5)Y)Pt((C_2H_5)_3)_2]$ (1a, X=Y=H; 1b, X=Y=Cl; and 1c, X=H, Y=Cl),[3] the planar transition metal-silyl four-membered rings of the form $M_2L_nL_m(SiR_2)_2$ are characterized by long Si-Si distances, short M-M distances (Table I), and acute M-Si-M angles.[5-11] The consistency of the M-Si-M (70-75°) and Si-M-Si (105-110°) angles in this type of structure is remarkable in light of the variety of metals, ligands, and silyl substituents present in these complexes. The two exceptions possess two different structures. In the complex $Ti_2(C_5H_5)_4H_2(Si(C_6H_5)H)_2$, the ring is roughly rectangular with no short cross-ring distances. The complexes 1a-c possess short cross-ring Si-Si distances (within the known range of Si-Si bonds)[3], long M-M distances, and acute Si-M-Si angles.[12] The short cross-ring Si-Si distances observed in the $[R_2SiX]_2$ four-membered rings, where X is a bridging main group moiety[13], have been discussed in terms of electron pair repulsions on X atoms, strong Si-X bonds, and

2

unsupported Si-Si $\pi$-bonds.[14]   The nature of Si-Si bonding (if

any) in the transition metal silyl four-membered rings with short

Si-Si distances and the role of metal d electrons have, to our

knowledge, not been addressed before.   In particular, this  study

probes whether or not the complexes with short Si-Si cross-ring

distances can be described as disilenes bound to two metal

centers.   The recent observation that bulky disilenes can form

complexes with single metal centers,[15] and the conclusion of a

theoretical study that a disilene should be a better $\sigma$-donor and

$\pi$ acceptor than an alkene,[14a] lend support to the proposed

description.

A molecular orbital study is made of two complexes (Fig. 1).

The first, $Mn_2(CO)_8(Si(C_6H_5)_2)_2$,[7] has Mn-Mn and Si-Si distances

of 2.871 and 3.852 Å, respectively.   The second one,

$Pt_2((C_2H_5)_3P)_4(Si(C_6H_5)Cl)_2$, (1b) has respective Pt-Pt and Si-Si

distances of 3.973 and 2.602 Å.[3]   In the Mn complex the metal-

metal distance is close to the sum of two atomic radii, just 0.17

Å greater, and the Si-Si distance is much larger than the bulk

single bond distance of 2.35 Å.[16]   In the Pt complex the metal-

metal distance is much greater than the sum of two atomic radii,

2.78 Å, and the Si-Si distance is just 0.25 Å greater than the

single bond value.   The theoretical evaluation of the metal-metal

and Si-Si bond orders is an important aspect of the present

study.

The atom superposition and electron delocalization molecular

orbital (ASED-MO) theory[17,18] is used.   Because the experimentally

determined equilibrium structures are available, no structure

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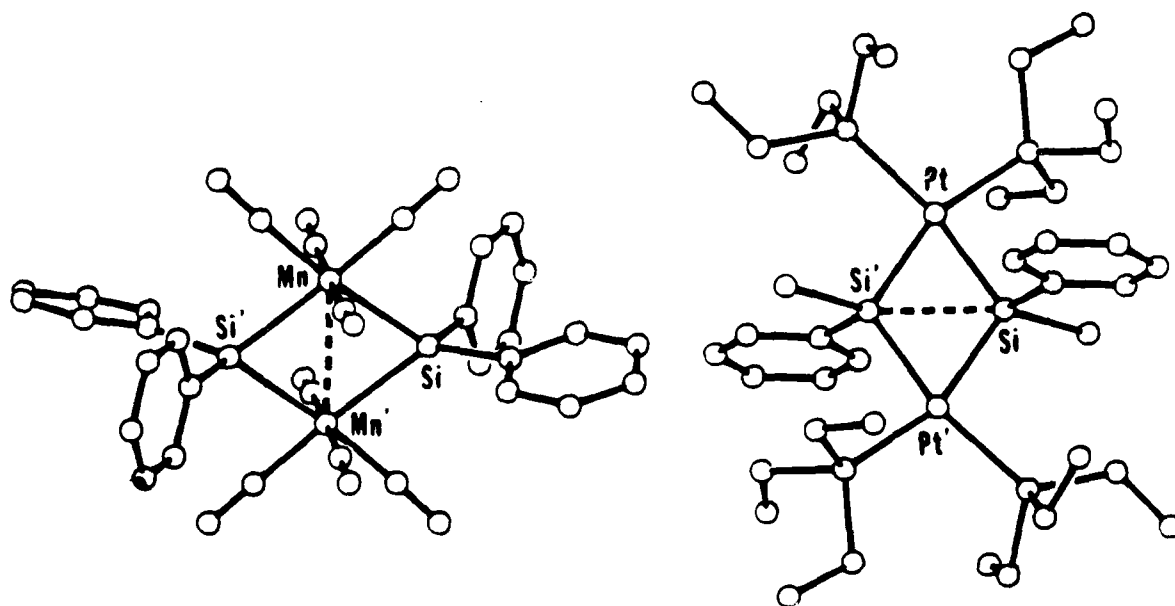
1. Structures of $Mn_2(CO_8(Si(C_6H_5)_2$ and $Pt_2(P(C_2H_5)_3)_4$
   $(Si(C_6H_5)Cl)_2(1b)$.

optimizations are required. The analysis is based on a molecular orbital correlation diagram for each complex. The complete Mn complex is employed in the calculation and the Pt complex is simplified by replacing the 12 Et groups attached to the two P atoms by 12 H atoms. The ASED-MO parameters, which are taken from the literature as discussed in Ref. 18, are given in Table II.

Bonding of the Mn complex is examined first. The bonding together of the $[Si(C_6H_5)_2]_2$ and $[Mn(CO)_4]_2$ fragments is shown in the correlation diagram of Fig. 2. Examination of the ten 3d molecular orbital energy levels for $[Mn(CO)_4]_2$ reveals three empty orbitals, one of which is Mn-Mn bonding while the other two are antibonding. Each Mn is $d^7$. Altogether, four bonding orbitals and three antibonding orbitals are occupied, so the formal metal bond order of the fragment is 1. The relatively short Mn-Mn bond forces a long Si-Si distance for optimal Si-Mn bonding overlap. Because of the large Si-Si distance, the $\sigma-\sigma^*$ and $\pi-\pi^*$ splittings are very small, so the fragment could be viewed as two weakly interacting silylene molecules. Nevertheless, $\sigma$ and $\pi$ notation is used. As the diagram shows, the Mn disilene $\sigma$, $\sigma^*$, $\pi$, and $\pi^*$ (or the four silylene lone pair and empty p orbitals) all have bonding overlaps with metal fragment orbitals, giving a substantial Si-Mn Mulliken overlap population of 0.27. Because the disilene fragment is a 4 electron donor, only the 3d $\sigma^*$ orbital remains empty so the Mn-Mn bond order is still 1 and each Mn becomes $d^9$.

Now consider the bonding in the Pt complex 1b shown in Fig. 3. In the $Pt_2$ fragment all ten d molecular orbitals are occupied,

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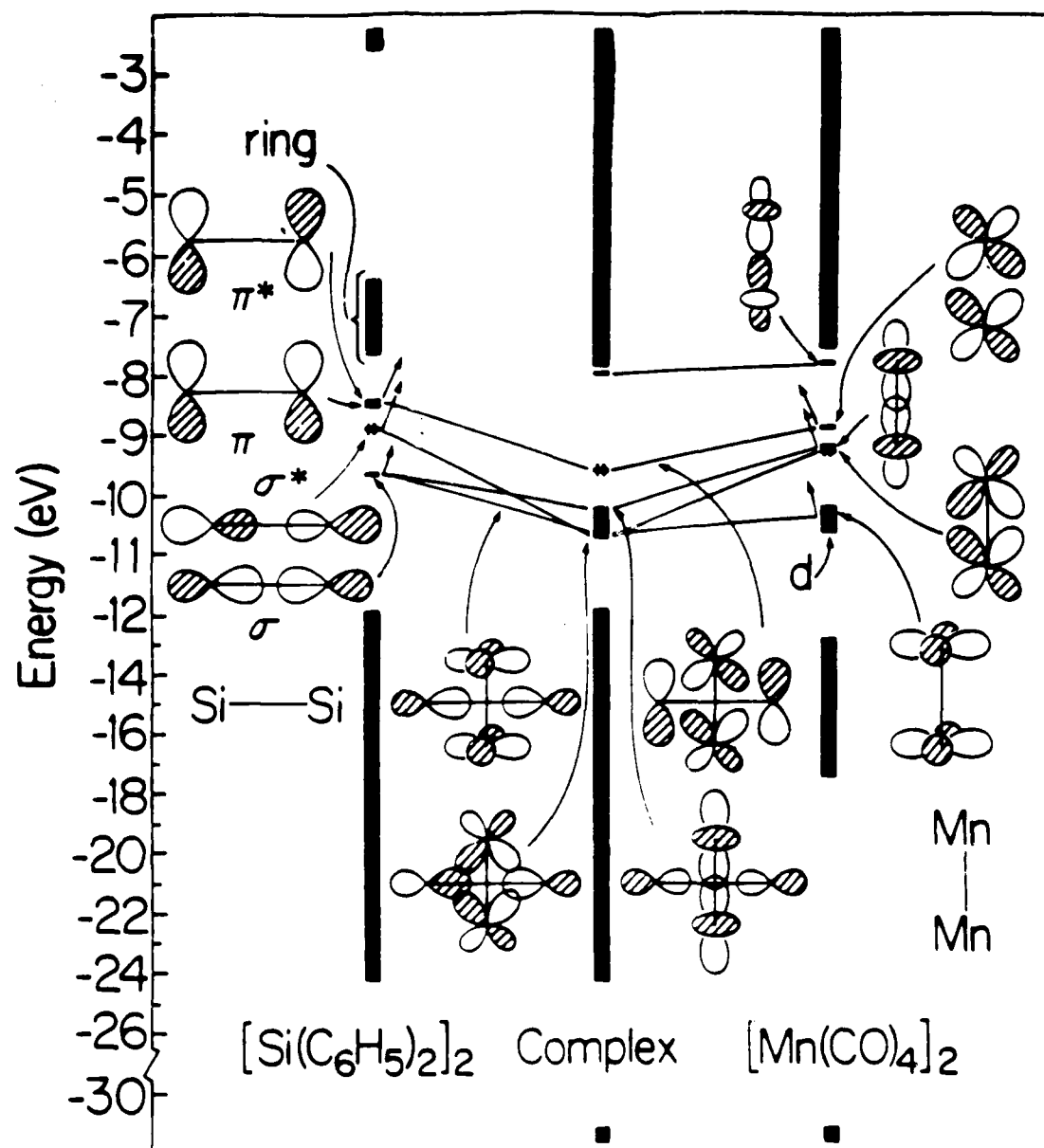
2. Bonding of disilene to Mn₂ dimer.
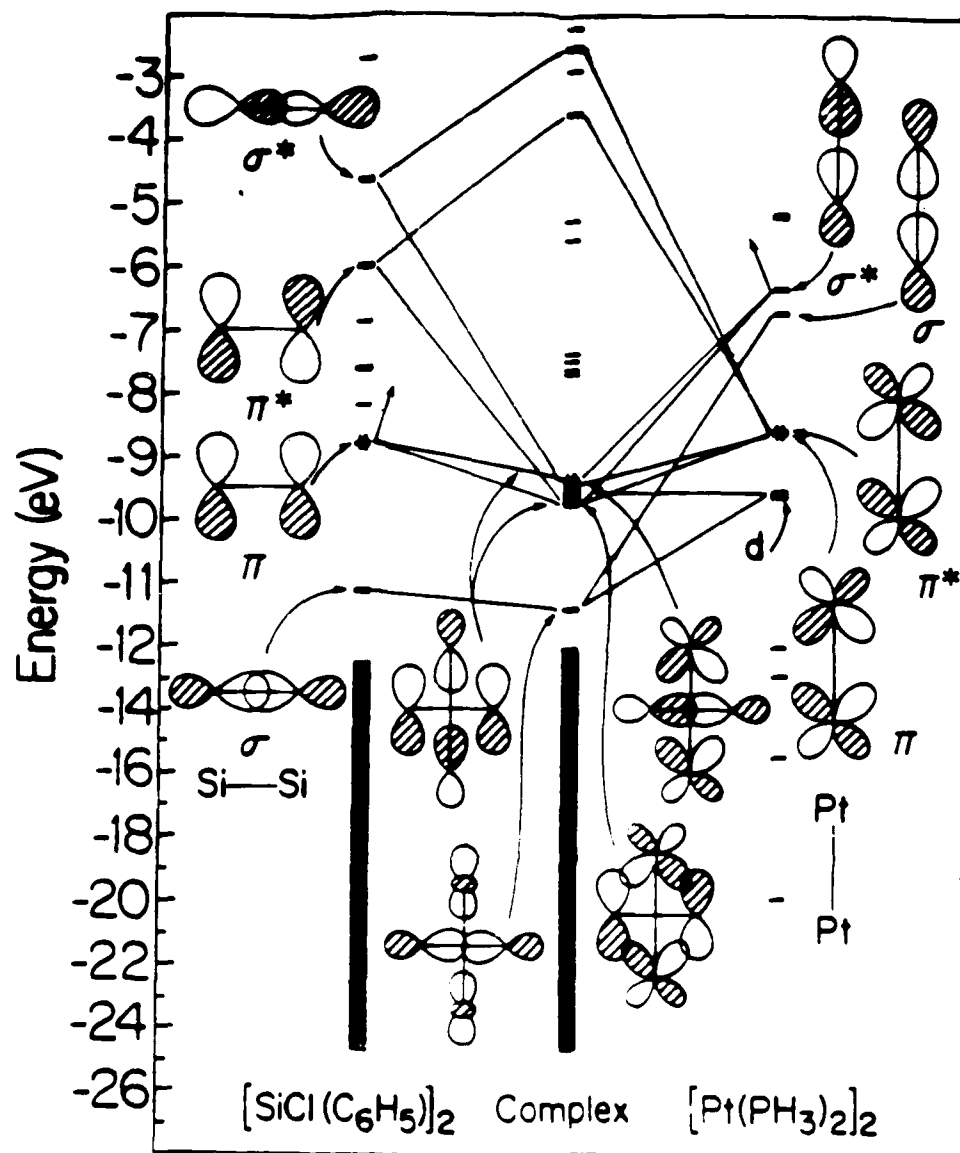
3. Bonding of disilene to Pt₂ dimer.

so the Pt-Pt bond order is 0 and each Pt is $d^{10}$. The Si-Si bond is intact in this complex because this structure allows strong Si-Pt bonding overlap and the $\sigma$ and $\pi$ electronic structure shows the expected splittings. Note that the empty $\sigma_S$ and $\sigma_S^*$ orbitals in the $Pt_2$ fragment lie low in energy and are accessible for bonding to the $Si_2$ fragment. In the complex the Si-Si $\pi$ orbital donates to the Pt-Pt $\sigma_{sp}^*$ orbital and the Si-Si $\sigma$ orbital donates to the Pt-Pt $\sigma_{sp}$ orbital; these donation interactions have no net influence on the Pt-Pt bond order. There is some back-donation from the $Pt_2$ fragment d set to the Si-Si $\pi^*$ and $\sigma^*$ orbitals. The Si-Si Mulliken overlap population for 1b is 0.27 and the Si-Pt overlap population is 0.52, indicating strong Si-Si and Si-Pt bonding. The Pt-Pt bond order remains 0, which explains the long Pt-Pt distance, and each Pt remains $d^{10}$.

Based on these two studies, generalizations to the other metal-silyl four-membered rings are possible. Consider the number of d electrons on each M of the $M_2$ fragments for the remaining complexes in Table I: $Pt_2(P(C_6H_{11})_3)_2H_2(Si(CH_3)_2)_2[d^9]$; $Ru_2(Si(CH_3)_3)_2(CO)_6(Si(CH_3)_2)_2$ $[d^7]$; $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2[d^6]$; $W_2(CO)_8H_2(Si(C_2H_5)_2)_2[d^5]$; $Re_2(CO)_6H_4(SiC_2H_5)_2[d^5]$; $Ti_2(C_5H_5)_4H_2(Si(C_6H_5)H)_2$ $[d^1]$. According to Fig. 3 the first Pt complex has a Pt-Pt bond order of 1 because the $\sigma_{sp}^*$ becomes the LUMO, so there is a short Pt-Pt distance. The Ru complex has a metal bond order of 1 like the Mn complex and the first Re complex has a metal bond order of 2 while the other Re and the W complexes have a metal bond order of 1, as may be seen in Fig. 2. In the Ti complex all distances are long and it is expected that the 1s

orbitals of the two H atoms, which bridge opposing Si-Ti bonds, stabilize the Ti-Ti d-d $\pi^*$ + Si-Si p-p $\pi^*$ orbital so that it is occupied. This ensures long Si-Si and Ti-Ti distances and at the same time provides Si-Ti bonding.

Complexes with $d^8$ metal centers in the $M_2$ fragments present an interesting situation. According to Fig. 2 the fragment M-M bond order will be 2 but in the complex it will be 0. Thus a short M-M bond seems to be excluded, and therefore the Fe-Fe distance in $Fe_2(CO)_8(Si(C_6H_5)_2)_2$ is likely to be long. This complex has been made but not structurally characterized.[19]

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Commun., in press.  The Si-Si separation in both complexes
is $\leq$ 2.75 Å.

12. a.  The complex $Ti_2(C_5H_5)_2(SiH_2)_2$ also possesses a short
cross-ring Si-Si distance (2.69 Å) and an acute Si-M-Si
angle.[12b]  The report of this complex provided no details on
how the hydrides on silicon were located and no data other
than elemental analyses for the presence or number of these
hydrides.  Because this complex is much less well charac-

terized than other metal-silicon four-membered rings, we have chosen not to include it in discussions of bonding.

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# Figure Captions

1. Structures of $Mn_2(CO_8(Si(C_6H_5)_2$ and $Pt_2(P(C_2H_5)_3)_4$
   $(Si(C_6H_5)Cl)_2(1b)$.

2. Bonding of disilene to $Mn_2$ dimer.

3. Bonding of disilene to $Pt_2$ dimer.

Table I. Structures of transition metal-silyl four-membered rings based on data in references 1-8. d electron count is for M in $M_2$ fragment.

| Compound | Reference | $d^n$ | distance (Å) | | angle (deg) | |
|---|---|---|---|---|---|---|
| | | | M-M | Si-Si | Si-M-Si | M-Si-M |
| $Pt_2(C_2H_5)_3P)_4(Si(C_6H_5)Cl)_2$ | 3 | $d^{10}$ | 3.973 | 2.602 | 67 | 114 |
| $Pt_2(P(C_6H_{11})_3)_2H_2(Si(CH_3)_2)_2$ | 5 | $d^9$ | 2.708 | 3.896 | 110 | 70 |
| $Ru_2(Si(CH_3)_3)_2(CO)_6(Si(CH_3)_3)_2$ | 6 | $d^7$ | 2.959 | 3.886 | 105 | 75 |
| $Mn_2(CO)_8(Si(C_6H_5)_2)_2$ | 7 | $d^7$ | 2.871 | 3.852 | 107 | 73 |
| $Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$ | 8 | $d^6$ | 3.052 | 4.075 | 106 | 74 |
| $Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$ | 9 | $d^5$ | 3.084 | 4.023 | 105 | 75 |
| $W_2(CO)_8H_2(Si(C_2H_5)_2)_2$ | 10 | $d^5$ | 3.183 | 4.225 | 106 | 74 |
| $Ti_2(C_5H_5)_4H_2(Si(C_6H_5)H)_2$ | 4a | $d^1$ | 3.890 | 3.820 | 88 | 91 |
| | | | | | 89 | 90 |

Table II. Valence orbital ionization potentials, IP(eV) and Slater exponents, ζ (a.u.) used in the ASED-MO calculations.

| atom | n[a] | s IP | ζ | n | p IP | ζ | n | d IP | ζ₁ | c₁[b] | ζ₂ | c₂[b] |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
| | | | | | | | | | $\zeta_1$ | $c_1^b$ | $\zeta_2$ | $c_2^b$ |
| Mn | 3 | 7.434 | 1.65 | 4 | 5.15 | 1.35 | 3 | 9.0 | 5.15 | 0.5139 | 1.70 | 0.6929 |
| Pt | 6 | 9.0 | 2.55 | 6 | 4.96 | 2.25 | 5 | 9.6 | 6.013 | 0.6559 | 2.396 | 0.5715 |
| S | 3 | 13.46 | 1.634 | 3 | 8.15 | 1.428 | | | | | | |
| P | 3 | 16.15 | 1.881 | 3 | 10.49 | 1.629 | | | | | | |
| Cl | 3 | 24.54 | 2.356 | 3 | 12.97 | 2.039 | | | | | | |
| O | 2 | 28.48 | 2.246 | 2 | 13.62 | 2.27 | | | | | | |
| C | 2 | 16.59 | 1.658 | 2 | 11.26 | 1.618 | | | | | | |
| H | 1 | 13.6 | 1.2 | | | | | | | | | |

[a]Principal quantum number.

[b]Linear coefficients for double-zeta d Slater orbitals.