We have seen exactly this process in earlier work with cyclopolyarsine reactions of $M_2(CO)_{10}$ (M = Mn and Re),[7] in which a chain of eight CH_3As groups loses just one methyl group to form a trishomocubane structure to satisfy the electronic requirements of the Re atom to which the naked As atom is attached. There is at present insufficient evidence to determine whether the essential difference between Cp and Cp* precursors are sterically determined, a function of the M–M bond order, or both. We are currently studying comparable reactions of $[CpMo(CO)_2]_2$ and $[Cp^*Mo(CO)_3]_2$ to examine these factors. Our preliminary results suggest that the M≡M bond order may prove more important.[25] This would suggest that when the metal precursor is triply bonded, decarbonylation no longer competes with loss of organic substitution in the arsenic precursor. Initial metal–arsenic coordination occurs more rapidly at the coordinatively unsaturated metal centers in the triply bonded precursors promoting metal–metal bond scission, fragmentation of the cycloarsines, and loss of organic substitution.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 122270-44-4; 2, 122270-45-5; $[Cp^*W(CO)_2]_2$, 70634-77-4; *cyclo*$(CH_3As)_5$, 20550-47-4; $[Cp^*Mo(CO)_2]_2$, 12132-04-6; *cyclo*$(PhAs)_6$, 20738-31-2.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages); listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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[25] In fact, we may speculate that the low yield of M_2As_2 species from As_4 and As_4S_4 sources may be due to traces of the singly bonded metal precursor which accompany the preparation of $[Cp^*Mo(CO)_2]_2$.

Bonding in Transition-Metal–Silyl Dimers. Molecular Orbital Theory

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Received February 2, 1989

Molecular orbital studies of $Mn_2(CO)_8(Si(C_6H_5)_2)_2$ and $Pt_2(H_3P)_4(Si(C_6H_5)Cl)_2$ 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 the Si–Si bond intact, binds to the Pt atoms by means of ordinary π donation and back-donation to π^*. On the basis of 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/cat-

Table I. Structures of Transition-Metal–Silyl Four-Membered Rings Based on Data in Ref 1–8[a]

compd	ref	d^n	dist, Å M–M	dist, Å Si–Si	angle, deg Si–M–Si	angle, deg 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

[a] d electron count is for M in M_2 fragment.

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Table II. Valence Orbital Ionization Potentials, IP (eV), and Slater Exponents, ζ (au), Used in the ASED-MO Calculations

	s			p			d					
atom	n^a	IP	ζ	n	IP	ζ	n	IP	ζ_1	c_1^b	ζ_2	c_2^b
Mn	4	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
Si	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	2.227						
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-ζ d Slater orbitals.

alytic 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 $[((C_2H_5)_3P)_2Pt(Si(C_6H_5)X)(Si(C_6H_5)Y)Pt(P(C_2H_5)_3)_2]$ (**1a**, X = Y = H; **1b**, X = Y = Cl; **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. 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 unsupported Si–Si π-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 σ donor and π acceptor than an alkene[14a] lend support to the proposed description.

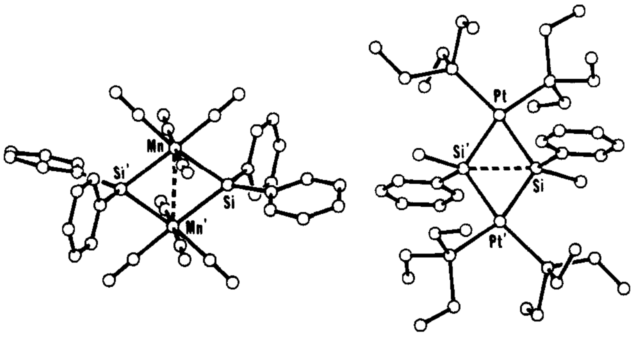

Figure 1. Structures of $Mn_2(CO)_8(Si(C_6H_5)_2)_2$ and $Pt_2(P(C_2H_5)_3)_4(Si(C_6H_5)Cl)_2$ (**1b**).

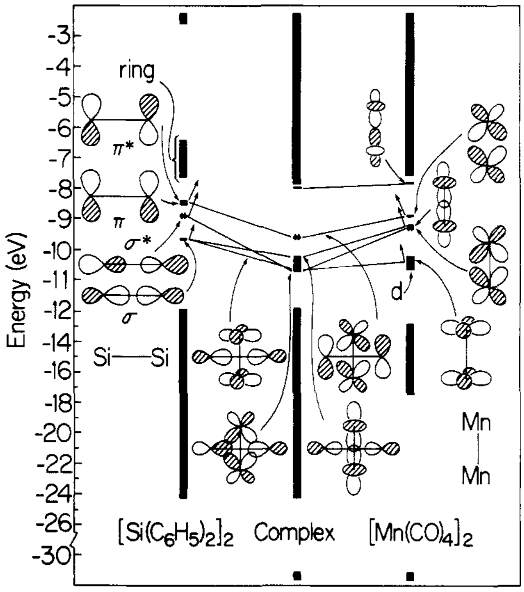

Figure 2. Bonding of disilene to Mn_2 dimer.

A molecular orbital study is made of two complexes (Figure 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.

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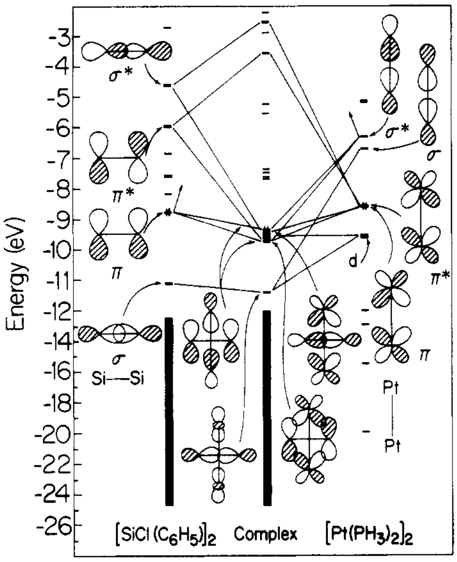

Figure 3. Bonding of disilene to Pt_2 dimer.

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 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 four 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 Figure 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 σ–σ^* and π–π^* splittings are very small, so the fragment could be viewed as two weakly interacting silylene moieties. Nevertheless, σ and π notation is used. As the diagram shows, the Mn disilene σ, σ^*, π, and π^* (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 four-electron donor, only the 3d σ^* 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 Figure 3. In the Pt_2 fragment all ten d molecular orbitals are occupied, 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 σ and π electronic structure shows the expected splittings. Note that the empty σ_s and σ_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 π orbital donates to the Pt–Pt σ_{sp}^* orbital and the Si–Si σ orbital donates to the Pt–Pt σ_{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 π^* and σ^* 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}.

On the basis of 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]; $Re_2(CO)_6H_4(Si(C_2H_5))_2$ [d^5]; $Ti_2(C_5H_5)_4H_2(Si(C_6H_5)H)_2$ [d^1]. According to Figure 3 the first Pt complex has a Pt–Pt bond order of 1 because the σ_{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 Figure 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 π^* + Si–Si p–p π^* 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 Figure 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]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Naval Research for support of this work.

Registry No. **1b**, 113999-67-0; $Mn_2(CO)_2[Si(C_6H_5)_2]_2$, 40764-56-5.

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