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Small Ring Metallo-cycles. 4.¹ Synthesis and Chemical Reactivity of *cyclo*-Metalladisiloxanes, $\overline{\text{MSiR}_2\text{OSiR}_2}$, and *cyclo*-Metalladisilabutanes, $\overline{\text{MSiR}_2\text{CH}_2\text{SiR}_2}$

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Abstract: The new metallo-cycles, $\text{L}_2\text{Pd}(\text{Si}_2\text{Me}_4\text{O})$, $\text{L}_2(\text{CO})(\text{H})\text{Ir}(\text{Si}_2\text{Me}_4\text{O})$, $\text{L}_2(\text{CO})(\text{H})\text{Ir}(\text{Si}_2\text{Me}_4\text{CH}_2)$, $\text{L}_2\text{Pt}(\text{Si}_2\text{Me}_4\text{CH}_2)$, and $\text{L}_2\text{Pd}(\text{Si}_2\text{Me}_4\text{CH}_2)$ ($\text{L} = \text{Ph}_3\text{P}$), have been prepared and characterized. The metallo-cycles contain the four-membered ring, $\overline{\text{MSiXSi}}$ ($\text{X} = \text{O}, \text{CH}_2$). Wilkinson's catalyst, L_3RhCl , also reacts with tetramethyldisiloxane to give an unstable metallo-cycle which is postulated to be dinuclear. These new complexes have been shown to act as catalysts for the disproportionation of tetramethyldisiloxane into dimethylsilane and linear polysiloxanes in neutral milieu at room temperature. The rhodium metallo-cycle gives, in addition, cyclic polysiloxanes. This disproportionation involves the breaking and re-forming of strong Si-O bonds. A mechanism is proposed in which the four-membered ring cleaves to form an intermediate with coordinated silylene and silaketone. It is postulated that relief of angle strain in the four-membered ring is the driving force for the cleavage of the Si-O bond, and hence is responsible for the catalytic activity observed for the metallo-cycles. The scission of the four-membered metallo-cycle is similar to that postulated for metallo-cyclobutanes in the catalysis of the olefin metathesis reaction.

Introduction

Small-ring metallo-cycles have been implicated as intermediates in a large number of reactions catalyzed by transition metal complexes. Thus, metallo-cyclobutanes are postulated to play a key role in the catalysis of the olefin metathesis reaction.²⁻⁸ Metallo-cycles are also implicated in various ring openings and rearrangements,⁹⁻¹¹ cyclooligomerizations of olefins,¹²⁻¹⁵ the polymerization of silacyclobutanes,^{16,17} and the addition of acetylenes to strained Si-Si bonds.¹⁸⁻¹⁹ In many instances, the metallo-cycles may be isolated.^{17,20}

In spite of their apparent ubiquity in many important reactions, very little is known about the chemistry of small-ring metallo-cycles. A metallo-cyclobutane, for example, could react by reductive elimination of cyclopropane, β -elimination to give propene, scission to give coordinated carbene and olefin, or

insertion of other small molecules into the metal-carbon bond. The oxidation state, coordination number, and electron configuration of the metal and the nature of the ancillary ligands could all affect the reactivity of the metallo-cycle and change the course of its reactions. Indeed, some platinacyclobutanes may be caused to give propene or cyclopropane, depending on the nature of added ligands.²¹ We have begun a program to study the synthesis and chemistry of small-ring metallo-cycles so that the nature of their reactivity may be better understood. A better understanding of metallo-cycle reactivity should allow a more rational design of catalysts for transformations involving metallo-cycles.

In this paper, we report some of our initial studies on *cyclo*-metalladisiloxanes and disilametallacyclobutanes, metallo-cycles which could show some interesting reactivity as

a result of ring strain. Prior to our work,^{1b} only one *cyclo*-metalladisiloxane, L₂Pt(Si₂Me₄O), had been reported.²²

Experimental Section

All synthetic manipulations were performed under nitrogen using Schlenk-ware techniques. Mass spectra of solids were obtained on an AEI 901 spectrometer, and GC-MS spectra of liquids were run on a Du Pont Dimispec 321 instrument (column: OV-17 liquid phase on acid-washed Chromosorb W support). IR spectra were determined on a Perkin-Elmer 457 spectrometer. ¹H NMR were obtained on Varian A-60 or Jeolco JNM-PS-100 spectrometers, the latter operating in the pulsed mode for detecting weak signals. 1,1,3,3-Tetramethyldisiloxane (TMDS) was a gift from the Dow Corning Corp. and was distilled prior to use. The platinum complexes used as starting materials were prepared by literature procedures.²³⁻²⁵ Analytical data are presented in Table I. Unless otherwise indicated, L = Ph₃P. L₂Pt(Si₂Me₂O) was prepared by Eaborn's method.²²

2,4-(2,4-Dimethyl-2,4-disilapentanedyl)bis(triphenylphosphine)-platinum(II), L₂Pt(Si₂Me₄CH₂). The complex L₂Pt(C₂H₄) (0.2 g, 0.3 mmol) was dissolved in 10 mL of benzene and bis(dimethylsilyl)methane (BDSM, 0.04 g, 0.3 mmol) added to the solution which was then refluxed for 2 h. After reflux, the benzene was pumped off, leaving a yellow-brown powder which was washed with petroleum ether, then redissolved in a minimum amount of benzene. Petroleum ether was added to the point of incipient crystallization. On standing, the yellow product, mp 130 °C, deposited, yield 40%.

1,3-(1,1,3,3-Tetramethyldisiloxanedyl)bis(triphenylphosphine)-palladium(II), L₂Pd(Si₂Me₄O). A. Tetrakis(triphenylphosphine)palladium(0)²³ (0.2 g, 0.2 mmol) in 10 mL of benzene was mixed with TMDS (0.04 g, 0.3 mmol) and the mixture refluxed for 12 h. The volume of the solvent was reduced to ca. 5 mL and petroleum ether added. The mixture was cooled to 0 °C, giving a 10% yield of product, mp 142 °C.

B. To a slurry of L₂PdCl₂ (0.2 g, 0.3 mmol) in 10 mL of benzene was added 0.04 g (0.3 mmol) of TMDS and the mixture refluxed for 30 min, during which time the L₂PdCl₂ dissolves and the solution turns dark brown. Removal of all volatiles left a dark oil which was dissolved in a few milliliters of methylene chloride and chromatographed over Florisil. The first band to elute was L₂PdCl₂. With 10% acetone/methylene chloride, the product eluted as a yellow band. All solvent was removed and the product recrystallized from benzene/petroleum ether to give a 40% yield of yellow product.

2,4-(2,4-Dimethyl-2,4-disilapentanedyl)bis(triphenylphosphine)-palladium(II), L₂Pd(Si₂Me₄CH₂). This complex was prepared from L₂PdCl₂ (0.2 g, 0.3 mmol) and BDSM (0.04 g, 0.3 mmol) in the same manner as the above siloxane complex except that the reflux time was 1 h, and the purification procedure was identical. The yield of yellow product, mp 125 °C, was 25%.

Hydrido-1,3-(1,1,3,3-tetramethyldisiloxanedyl)carbonylbis(triphenylphosphine)iridium(III), L₂Ir(H)(CO)(Si₂Me₄O). To a slurry of Vaska's compound, L₂Ir(CO)Cl (0.6 g, 0.8 mmol), in 10 mL of benzene was added 0.2 g (1.5 mmol) of TMDS. After stirring at room temperature for 20 min, all the Vaska's complex had dissolved to give a colorless solution. The solvent was pumped away, leaving a white powder which was recrystallized from CH₂Cl₂/ethanol to give colorless crystals, mp 150–154 °C, yield 80%.

Hydrido-2,4-(2,4-dimethyl-2,4-disilapentanedyl)carbonylbis(triphenylphosphine)iridium(III), L₂Ir(H)(CO)Ir(Si₂Me₄CH₂). This complex was made in a manner analogous to that of the corresponding disiloxane complex by stirring Vaska's complex (0.5 g, 0.7 mmol) with BDSM (0.4 g, 3 mmol) in benzene for 2 h at room temperature. At the end of this time, the solvent was pumped away from the colorless solution, giving a white powder, mp 132–135 °C. Although the spectral properties leave little doubt of the nature of this complex, it is unstable and rapidly decomposes to L₂Ir(CO)H.²⁶

Reaction between L₃RhCl and TMDS. TMDS (0.08 g, 0.6 mmol) was added to a benzene slurry of L₃RhCl and the mixture stirred for 20 min at room temperature. After this time, the purple L₃RhCl had dissolved to give a yellow-orange solution. Complete removal of all volatiles at room temperature gave a yellow-orange powder, mp 135–140 °C. The complex decomposes in solution unless excess TMDS is present.

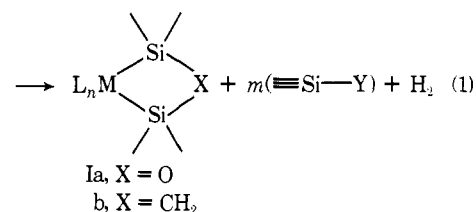
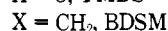
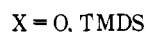
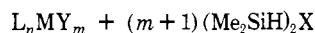
Hydrido-1,5-(1,1,3,3,5,5-hexamethyltrisiloxanedyl)carbonylbis(triphenylphosphine)iridium(III), L₂Ir(H)(CO)-Ir(Me₆Si₃O₂). To a slurry of 0.5 g (0.7 mmol) of Vaska's complex in 10 mL of benzene was added

0.2 g (0.9 mmol) of 1,1,3,3,5,5-hexamethyltrisiloxane (HMTS) and the solution refluxed for 2 h. During this time Vaska's complex dissolved completely to give a pale yellow solution. All the volatiles were pumped off and analyzed by GC-MS. In addition to starting trisiloxane, HMe₂SiOSiMe₂OSiMe₂Cl was shown to be present. The light yellow solid remaining in the reaction flask was washed with petroleum ether, recrystallized, and analyzed spectroscopically: IR ν (IrH) 2060, ν (CO) 1970, SiMe 1260, 800, ν (SiOSi) 1100 cm⁻¹; NMR Ph 7.2 (5), SiMe (0.6 and 0.5, 1:1) (1), (0.2 and 0.05, 1:1) (2). The latter two peaks were each split into doublets with $J = 2$ Hz (³¹PtSiMe).

Catalysis of Siloxane Oligomerization. Typically, a 100:1 ratio of siloxane to metallocycle was stirred in benzene solution at room temperature. Periodically, a sample was withdrawn and analyzed by GC-MS. No differences in product distribution were observed when the volatiles were first removed from the catalyst solution by trap to trap distillation before GC analysis. Also, no disproportionation of tetramethyldisiloxane alone was observed under the analysis conditions. Hence, the observed disproportionation does not occur as a result of heating in the GC inlet, etc. In several instances, the reactions were performed on a high-vacuum system and the Me₂SiH₂ produced was purified by trap to trap distillation and identified by comparison of its vapor-phase IR with that of an authentic sample. The mass spectra of the lower siloxane oligomers were compared with those of authentic samples. The spectra of linear and cyclic polysiloxanes were also analyzed by comparison to the reported spectra of permethylpolysilanes.²⁷ In addition, the isotope patterns for C_mSi_n were calculated and compared to the observed pattern as a check on the assignment.

Results and Discussion

The analytical and spectral data for the new complexes are presented in Tables I and II, respectively. The analytical and spectral data (see below) establish the complexes as metallocycles of type I.



The IR spectra of the metallocycles in the SiOSi region are particularly characteristic of the structure. Linear siloxanes usually absorb in the 1060–1080-cm⁻¹ range, as do the larger, unstrained cyclic oligomers, (OSiR₂)_n (n > 4). Cyclic trimers usually absorb around 1015 cm⁻¹.³² In the complexes Ia, the SiOSi absorption is split into two components, presumably the asymmetric and symmetric stretches, with frequencies of 1090–1070 and 1010–1030 cm⁻¹, respectively. The former is more intense.

Owing to its instability, the metallocyclobutane **7** was not analyzed. However, its spectral properties, especially the NMR, clearly establish its identity. The Si-methyl groups are nonequivalent, as found for the siloxane analogue **4**. The structure of **4** has been determined crystallographically and the reason for the nonequivalence of the Si-methyl groups is clear: one set is adjacent to the carbonyl ligand, and the other set adjacent to the hydride ligand.^{28,1b} The phosphine ligands are trans to the Si atoms.

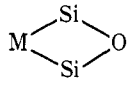
In all cases, the Si-methyl groups appear as a closely spaced doublet due to coupling with the trans phosphorus ($J = 2$ Hz). The coupling of the cis phosphorus is too small to resolve. In addition, the Pt complexes, **1** and **5**, show splittings of the Si-methyl protons from the ¹⁹⁵Pt nucleus ($J = 10$ Hz) which is present in 34% abundance. Thus, the Si-methyl region of **5**, L₂Pt(Si₂Me₄O), appears as an apparent triplet of doublets with

Table I. Analytical Data for Pt, Pd, and Ir Metalloacycles^a

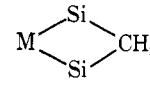
		C	H	P	Si	M
1, L ₂ Pt(Si ₂ Me ₂ CH ₂)	calcd: ^b	65.34	5.77	5.72	5.18	18.00
	found:	65.23	5.61	5.63	5.09	17.68
2, L ₂ Pd(Si ₂ Me ₄ O)	calcd: ^c	67.70	5.93	7.28	6.60	12.49
	found:	65.26	5.55	7.02	6.32	12.01
3, L ₂ Pd(Si ₂ Me ₄ CH ₂)	calcd: ^c	69.11	6.17	7.28	6.60	12.49
	found:	65.62	5.82	7.33	6.60	12.01
4, L ₂ (H)(CO)Ir(Si ₂ Me ₄ O)	calcd: ^d	55.95	5.31	6.61	6.07	20.84
	found:	55.84	5.23	6.81	6.10	20.93

^a L = Ph₃P. ^b Calcd for (complex·3C₆H₆). ^c Calcd for (complex·4/3C₆H₆). ^d Calcd for (complex·EtOH).

Table II. Spectral Data for Metalloacycles of Pt, Pd, Ir, and Rh



i



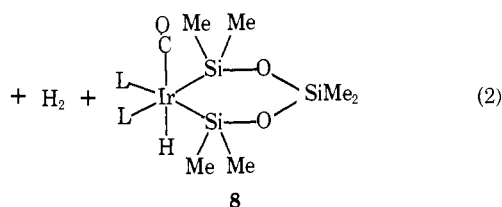
ii

A. Complexes i							
M	IR, cm ⁻¹			NMR			J, Hz
	SiMe	SiXSi	other	δ(Ph)	δ(Me)	δ(other)	
5, L ₂ Pt	1260	1090	430 (Pt-P)	7.2	-0.8		10 (¹⁹⁵ PtSiMe)
	790	1010	370 (Pt-Si)				
2, L ₂ Pd	1260	1090	450 (Pd-P)	7.2	0.0		2 (³¹ PtSiMe)
	800	1040	380 (Pd-Si)				
4, L ₂ (H)(CO)Ir	1240	1070	2060 (Ir-H)	7.2	0.2, 0.05	-8.2 (IrH)	2 (³¹ IrSiMe)
	840	1030	1950 (CO)				
6 L ₃ RhCl + TMDS	1250	1090		7.2	0.5 ^a		8 (³¹ IrH)
	800	1020					
B. Complexes ii							
1, L ₂ Pt	1230	1090 (w)	420 (Pt-P)	7.2	-0.2	0.4 (-CH ₂ -)	10 (¹⁹⁵ PtSiMe)
	820		370 (Pt-Si)				
3, L ₂ Pd	1260	1090 (w)	450 (Pd-P)	7.2	-0.1	-0.5 (-CH ₂ -) ^b	2 (³¹ PdSiMe)
	800		380 (Pd-Si)				
7, L ₂ (H)(CO)Ir	1240	1050	2060 (Ir-H)	7.2	-0.2, -0.3	0.2 (-CH ₂ -) ^b	2 (³¹ IrSiMe)
	820		1940 (CO)				

^a J(¹⁰³RhSiMe) < 1 Hz. ^b Unresolved multiplet.

an observed intensity ratio of ca. 1:4:1 (calcd, 1:3.9:1). The splittings in the methylene region of **1** were not resolved, possibly because of the poor signal to noise ratio (low solubility of the complex) and possibly because of a more complex splitting pattern. The latter could arise from coupling to the P atoms (which are now equivalent) and a lower coupling constant to ¹⁹⁵Pt. Similarly, the -CH₂- signal from **7** appears as an unresolved multiplet. One expects an AB quartet with each component split into a triplet from the two equivalent P atoms.

The spectral properties of the six-membered metalloacycle **8** are easily sufficient for its identification. Thus, the Ir-H and



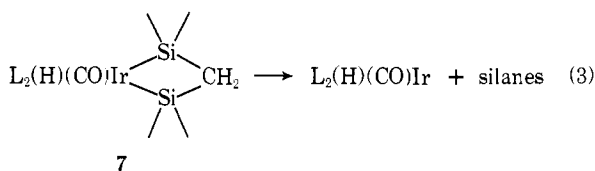
CO are established by IR and the silyl methyls appear as a set of four peaks in a 1:1:2:2 ratio at δ values of 0.6, 0.5, 0.2, and 0.05 ppm. These are assigned to the -OSiMe₂O- methyls at 0.6 and 0.5 ppm and the IrSiMe₂- methyls at the higher fields. In each set, the methyls are in nonequivalent environments as

with the complexes **4** and **7**. Furthermore, each signal due to the IrSiMe₂- methyls is split due to coupling with the trans phosphorus. The splitting of the SiOSi stretch, observed in the four-membered metalloacycles Ia, is absent in the six-membered ring complex.

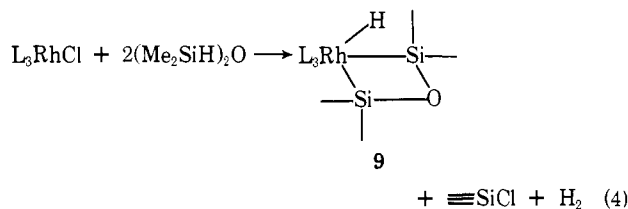
It is interesting to contrast the conditions for syntheses of the platinum and palladium metalloacycles. Although several Pt starting materials, e.g., L₄Pt, L₂Pt(CO₃), L₂PtCl₂, and L₂PtHCl, were tried, only L₂Pt(CO₃) gave a yield (90%) equivalent to that obtained with L₂Pt(C₂H₄). However, the carbonate route requires 16 h at room temperature compared to 30 min at reflux using the ethylene complex as a source of platinum. The dichloride, L₂PtCl₂, gave a 30% yield of metalloacycle after 5 h at 80 °C (benzene solution). Only starting materials were obtained after 3 days in refluxing benzene solution when L₂PtHCl was used as the Pt source. In contrast, L₂PdCl₂ is the reagent of choice for the synthesis of complex **2**. After a 20-min reflux period (benzene solution), the initially yellow mixture of L₂PdCl₂ and TMDS suddenly turns dark brown. Immediate workup gives a 40% yield of product. If the mixture is heated for any length of time after turning dark brown, the yield of metalloacycle drops rapidly. Also, no metalloacycle is present before the onset of the rapid darkening of the reaction mixture.

In all cases, the yields of the methylene-bridged metalloacycles (I, X = CH₂) were lower than those of the oxygen-bridged metalloacycles (I, X = O). It is generally observed that electronegative substituents, e.g., chlorine or oxygen, stabilize silicon-metal bonds. The stability of the iridium complex, **7**,

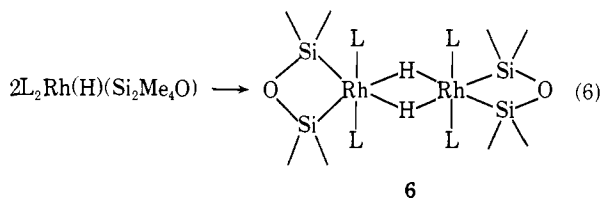
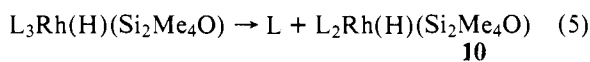
is so low that it cannot be isolated from solutions which do not contain an excess of BDSM. In solution, the complex rapidly decomposes to $L_2Ir(H)(CO)$ and unidentified silanes (eq 3).



Vaska's rhodium complex, $L_2Rh(CO)Cl$, fails to react with TMDS even after prolonged reflux in benzene solution. Wilkinson's catalyst, L_3RhCl , however, reacts rapidly with TMDS to give an unstable complex, **6**, the spectral properties of which establish it as a metallocycle of type Ia. No Rh-H stretch is observed in the IR, but a broad signal is observed in the bridging hydride region ($\delta -23.6$). By analogy with other reactions,³⁰ one might expect the product **9** (eq 4). However,



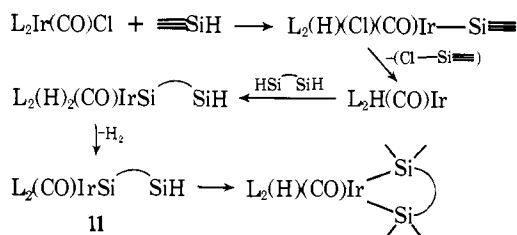
complex **9** may be so crowded that a triphenylphosphine dissociates to give a 16-electron complex, **10**, which dimerizes to give **6**. On the NMR time scale, the methyl protons of the rhodium complex, **6**, are equivalent. The structure tentatively assigned to **6** in eq 5 is consistent with all that is currently known about this unstable complex, including its catalytic properties (see below) and its chemistry. In particular, complex **6** rapidly absorbs carbon monoxide to give a complex which seems to be $L_2Rh(H)(CO)(Si_2Me_4O)$.³¹



The metallocycles formed from TMDS or BDSM and Pt(0), Ir(I), or Rh(I) undoubtedly form via a series of oxidative additions and eliminations (Scheme I).

Support for this scheme is the detection of H_2 and the appropriate chlorinated silane in the volatiles removed from the reaction mixture. Also, Eaborn et al.²² isolated the "open" intermediate corresponding to **11** when $L_2Pt(C_2H_4)$ was stirred at room temperature with TMDS. Heating the intermediate in benzene solution caused ring closure with the evolution of hydrogen to give **5**. However, the mechanism of the reactions of silyl hydrides with Pt(II) and Pd(II) complexes is probably not so straightforward. In particular, the odd behavior of

Scheme I



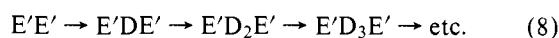
L_2PdCl_2 with TMDS or BDSM (see above) suggests that the metallocycle is formed in a rapid chain reaction following an induction period.

The effect of the metallocycles Ia on excess TMDS is remarkable in that catalytic amounts of these complexes induce a disproportionation of TMDS into dimethylsilane and higher polysiloxanes (eq 7). (Note: the notation $E' = Me_2HSiO_{1/2}$, $D = Me_2SiO$, will be used to describe polysiloxanes. Thus, $Me_2SiH(OSiMe_2)_3OSiHMe_2$ is $E'D_3E'$, $(OSiMe_2)_3$ is D_3 , etc.)

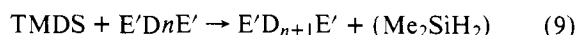


The platinum and palladium metallocycles, **5** and **2**, are inefficient catalysts in comparison to the iridium and rhodium complexes, **4** and **6**. The rates with the former are qualitatively lower, and the Pt and Pd complexes appear to decompose during the course of the reaction. The Ir and Rh complexes appear to be indefinitely active and may be recovered unchanged as long as excess TMDS is present in solution. When the concentration of TMDS is low relative to the concentrations of the higher oligomers, $E'D_nE'$, new peaks from as yet unidentified siloxanes appear on the GC trace and the original metallocycles cannot be recovered from solution.

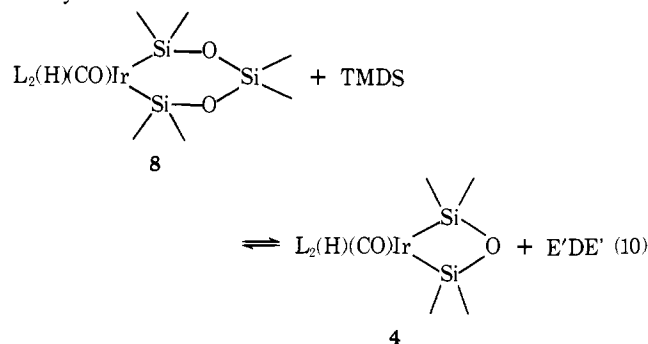
By monitoring the quantities of the various oligomers $E'D_nE'$ ($n = 1-6$) as a function of time, it was qualitatively established that the concentration of $E'DE'$ in the mixture rose rapidly in the first few minutes, then leveled off while the concentration of $E'D_2E'$ increased. After some $E'D_2E'$ is produced, $E'D_3E'$ appears and its concentration increases, etc. Thus, on a qualitative level, it appears that the oligomers are formed sequentially:



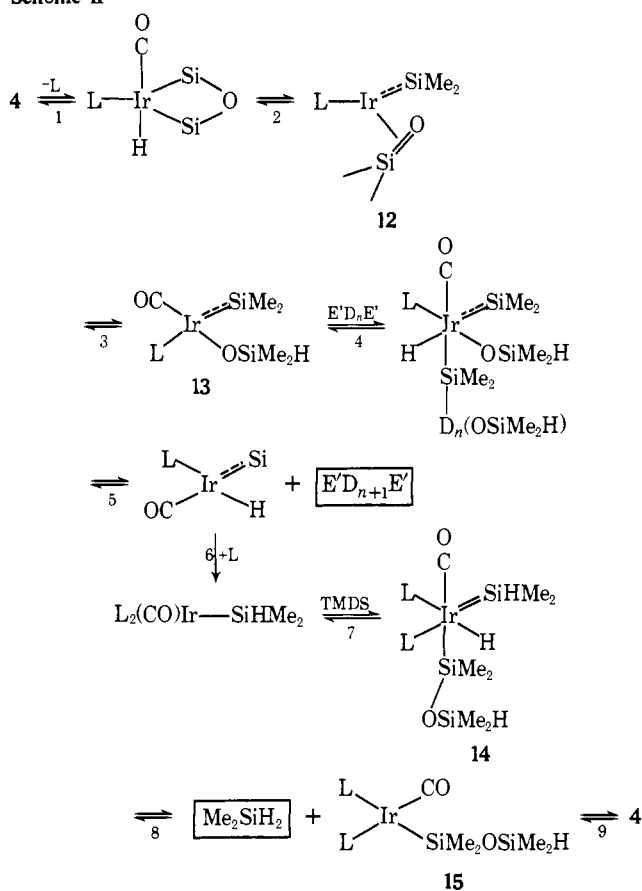
That the four-membered metallocycle is necessary for the disproportionation to occur was established by synthesizing the six-membered metallocycle, **8**. No reaction was observed when complex **8** was allowed to stir with excess hexamethyltrisiloxane. Two milliliters of hexamethyltrisiloxane, $E'DE'$, containing about 1 mol % of TMDS, was added to ca. 0.1 mmol of Vaska's complex in 10 mL of benzene. After stirring at room temperature for 2 h, no TMDS remained in the mixture. The only siloxanes present were $E'DE'$ and $E'D_2E'$, and the latter's concentration was equal to the initial concentration of TMDS. This experiment, in conjunction with the demonstrated inactivity of **8**, shows conclusively that TMDS generates the active disproportionation catalyst with Vaska's complex, and that the higher siloxanes are formed by the reaction



(No attempt was made to trap the dimethylsilane in this instance owing to the small amount produced.) This experiment also shows that either TMDS reacts much faster with Vaska's complex than does $E'DE'$ (even though the latter was in large excess) or that TMDS can react with **8** to form **4**, the active catalyst:



Scheme II



A mechanism, consistent with all the data in hand, for the catalysis of the siloxane disproportionation is presented in Scheme II. In step 1 we postulate a dissociation of phosphine to give a 16-electron Ir(III) species. In step 2, the four-membered ring breaks open to give a coordinated silylene, analogous to a coordinated carbene, and a coordinated silaketone. In step 3, the coordinated hydride shifts to the silicon of the silaketone to give a four-coordinate Ir(I) complex, **13**. Complex **13** can then oxidatively add to the Si-H bond of a siloxane oligomer, $E'D_nE'$. Reductive elimination (step 5) then occurs to give an Ir(I) hydride and the next higher oligomer, $E'D_{n+1}E'$. Association of the phosphine ligand in step 6 causes a hydride shift to the silylene, giving an Ir(I)-silyl complex which can add to the Si-H bond of TMDS (step 7). Complex **14** then eliminates dimethylsilane to give **15** which can undergo ring closure to regenerate the catalyst, **4**.

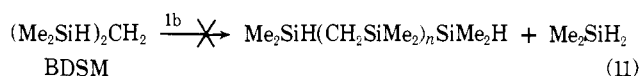
This proposed mechanism is noteworthy in several respects. The scission of the four-membered ring is analogous to the postulated scission of metalocyclobutanes to give coordinated carbene and olefin in the olefin metathesis reaction²⁻⁸ Although no stable metal silylene complexes are known, the stability of the divalent state increases with atomic number in group 4 and stable germylene and stannylene complexes are known.³²⁻³⁵ Silaketones have also been demonstrated as highly reactive intermediates.^{36,37} We propose that the strain present in the four-membered ring of **4** provides the driving force for the scission of the ring. This view is buttressed by the structural details of **4**.²⁸ In any event, strong Si-O bonds are broken and re-formed in a neutral milieu at room temperature in the observed disproportionation.^{38,39} Steps 2-5 of Scheme II seem reasonable in view of the mild conditions and the apparent necessity of the presence of the four-membered metalocycle for catalysis (see above).

The mechanism in Scheme II also accounts for the sequential formation of the oligomers (eq 8 and 9). At the start

of the reaction, the only silyl hydride present is TMDS (= $E'E'$). TMDS adds to **13** in step 4, producing $E'DE'$ in step 5. As its concentration increases, $E'DE'$ can compete with TMDS in step 4, producing $E'D_2E'$ in step 5, and so on. Some TMDS must be present in solution to regenerate the catalyst in step 7. Even if some higher oligomer, $E'D_nE'$, reacts in place of TMDS in step 7 to give an inactive complex, active complex **4** could still be regenerated provided that the reactions are reversible (cf. eq 10). There are several facets of the proposed mechanism which are amenable to experimental testing, e.g., kinetics, inhibition, crossover experiments, reversibility, etc. Such work is in progress and will be reported later.

Another interesting aspect of our observations to date concerns the rhodium catalyst, **6**. This catalyst, and one other which also appears to be dimeric,³¹ are the only ones which give cyclic oligomers, D_3 and D_4 , in addition to linear oligomers in the disproportionation of TMDS. In a dimeric catalyst, two silaketones may become coordinated on adjacent metal centers and couple to form the highly reactive dimer, D_2 . This four-membered ring may have a sufficient lifetime in a neutral solution to interact with a third, coordinated silaketone to give D_3 . D_3 is also strained and can add another silaketone to form D_4 ,^{36,37} or two D_2 units could dimerize to give the D_4 .

To date, we have not observed oligomerization of BDSM by the metalocycles Ib. Thus, stirring complex **7** with excess BDSM for 24 h failed to give any polysilmethylenes.



In conclusion, small-ring silicon-transition metal metalocycles have been synthesized and shown to be catalysts for the disproportionation of TMDS. This latter reaction may prove to have technological implications in that new types of silicone polymers are conceivable as a result of the neutral reaction media and the possible stereochemical control exerted by the metalocycle intermediates. All facets of this new area are currently under investigation.

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Binuclear Copper(II) Complexes as Mimics for Type 3 Coppers in Metalloenzymes. 1. The Importance of Cooperative Interactions between Metals in the Reversible Multielectron Transfer in Bis(1,3,5-triketonato)dnicopper(II) Complexes

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Abstract: The electrochemistry of several bis(1,3,5-triketonato)dnicopper(II) complexes that have magnetic and spectral properties similar to type 3 coppers in metalloenzymes has been investigated. Experimentally, these complexes adhere to the usual criteria for reversibility, have diffusion constants typical of two-electron transfer, have cyclic voltammographs with 42-mV peak separations, and give polarographic $\log(i/i_d - i)$ vs. E plots with 46 ± 3 mV slopes. Also, the quantitative addition of two electrons per molecule is proven by controlled potential electrolysis. All of these facts are consistent with the two-electron reversible reduction of the Cu(II),Cu(II) complex to a Cu(I),Cu(I) product in which the electrons are added sequentially at the same potential. The net result is a single-potential, two-electron transfer. The importance of cooperative interactions between the metals, the magnetic interactions, the structural parameters, and the substituent groups is discussed. It is thought that the redox reactions of type 3 coppers involve two-electron transfer. Therefore, the observed redox properties together with the magnetic and spectral properties make the bis(1,3,5-triketonato)dnicopper(II) complexes potential mimics for type 3 coppers in metalloenzymes.

Introduction

A number of multicopper proteins have been proven to contain pairs of copper atoms which in the cupric ions are strongly antiferromagnetically coupled. The better known examples include tyrosinase,¹⁻³ hemocyanin,³⁻⁶ laccase,⁶⁻⁸ ceruloplasmin,^{9,10} and ascorbate oxidase.¹¹⁻¹³ The coppers bound in this manner within the protein are commonly referred to as type 3 coppers and are characterized by lack of an EPR signal in both the oxidized and reduced states, an absorption band at about 330 nm, a relatively positive reduction potential for the process $[\text{Cu(II)}]_2 \rightarrow [\text{Cu(I)}]_2$ in which two electrons are transferred, and a large antiferromagnetic coupling constant. The chemical and physical properties of the multicopper proteins have recently been reviewed by Fee.¹⁴

No information is yet available on the coordination geometry or the nature of the donor atoms in type 3 copper centers. However, the lack of any abnormal spectral properties asso-

ciated with the oxidized form $[\text{Cu(II)}]_2$ argues strongly against unusual coordination geometry.^{2,15} There may be a significant difference between the structural details of the type 3 coppers from one metalloenzyme to another as evidenced by differences in chemical reactivity¹⁴ and the resting oxidation state of the deoxyenzymes.^{2,6} It is not clear at this stage whether these differences are due to the detailed configuration of the enzyme or to differences in structure and bonding about the type 3 copper atoms.

Since no structural information is available, the nature of the bridging system that gives rise to the strong antiferromagnetic interaction is not known. Several recent papers dealing mainly with EPR data for partially reduced and NO substituted systems have been concerned with structural aspects such as Cu-Cu distance.^{2,3,15-17} However, at this stage no entirely consistent understanding has emerged.

It is clear that low molecular weight copper complexes will