Table II. Change in Molecular Weight Distribution with Changing Conversion in a Typical Photopromoted (TMP)Rh-Catalyzed Polymerization Experiment[a]

conversion	M_n	M_w	M_w/M_n
6%	1.75×10^5	3.06×10^5	1.75
17%	2.18×10^5	3.93×10^5	1.80
37%	2.68×10^5	5.41×10^5	2.02
78%	1.44×10^5	3.98×10^5	2.76

[a] Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (M_w/M_n) values of poly(methyl acrylate) samples taken at different conversion levels.

benzene which was transferred via the vacuum line. After photolysis the sample was evacuated to dryness and subsequently redissolved in dry, degassed C_6D_6 (~3 mL). Inside an inert atmosphere box the solution was syringed into a volumetric flask together with an additional 3 mL dry degassed C_6D_6 and 4 mL of methyl acrylate. Methyl acrylate was chromatographed on grade I basic alumina to remove inhibitor and degassed prior to addition. The mixture was exposed to visible light, and 1-2-mL samples were removed during the polymerization process by use of a syringe. The conversion for each sample was determined by ^{1}H NMR, and subsequently the solutions were evacuated to remove excess methyl acrylate and benzene solvent. The polymer residue was redissolved in THF for GPC measurement. Results from using methods A and B were in substantial agreement.

GPC Results. A refractive index (RI) detector was used in determining the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and polydispersity (M_w/M_n) of each sample. The instrument was calibrated using monodispersed polystyrene standards. UV-vis detection ($\lambda = 420$ nm) was used to determine the presence of the (TMP)Rh units in the polymer.

In a typical polymerization experiment, 4-5 samples were analyzed with conversions varying from 5% to 80%. At conversions up to 40-50%, polydispersity was in the 1.4-2.0 range and M_w and M_n values increased with increasing conversion. At conversions greater than 50%, the polydispersity became significantly larger ($2 < M_w/M_n < 4$) with a parallel decrease in both M_w and M_n values of the samples (Table II). UV-vis detection at 420 nm indicated that a large portion of the (TMP)Rh units present in the system were attached to polymer chains but that some low molecular weight fragments containing (TMP)Rh occur at all stages of the polymerization.

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New Silane-Induced CO Activation in $[(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2{\cdot}THF]$: Formation of the Cyclic Bis(μ-carbyne) Complex $(\eta^5\text{-}H_3CC_5H_4)(CO)\overline{Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn}(CO)(\eta^5\text{-}H_3CC_5H_4)$ and the CC-Coupling Reaction of the Siloxy-Carbyne Ligands

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The labile complex $[(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2{\cdot}THF]$ (**6**) is generated by photolysis of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (**5**) and subjected to oxidative addition reactions with various silanes. With $(t\text{-}Bu)_2SiHCl$ (**7**) the cyclic bis(μ-carbyne) complex $(\eta^5\text{-}H_3CC_5H_4)(CO)\overline{Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn}(CO)(\eta^5\text{-}H_3CC_5H_4)$ (**8**) is formed in 15% yield. A systematic investigation of the product distribution in these reactions shows that the formation of bis(μ-carbyne) complexes versus silylmetal hydrides is a strong function of the substituents at the silane. Reaction of $[(\eta^5\text{-}EtMe_4C_5)Mn(CO)_2{\cdot}THF]$ (**19**) with **7** also gives, besides formation of the bis(μ-carbyne) complex $[(\eta^5\text{-}EtMe_4C_5)(CO)\overline{Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn}(CO)(\eta^5\text{-}EtMe_4C_5)]$ (**20**), the triply bridged carbonyl complex $(\eta^5\text{-}EtMe_4C_5)Mn(\mu\text{-}CO)_3Mn(\eta^5\text{-}EtMe_4C_5)$ (**22**). A single-crystal X-ray structure determination of **8** shows a cyclic four-membered ring structure with a bond distance Mn-C15 (carbyne C) of 1.857 (2) Å. The metallacycle is folded along the Mn-Mn bond (2.565 (1) Å) which is in accordance with an all-trans geometry of the ring substituents. This ring geometry opens up a reaction pathway for 1,3-cis elimination reaction of bis(siloxy)ethyne $[(t\text{-}Bu)_2HSiOC{\equiv}]_2$ (**9**) via a CC-coupling reaction of both carbyne units as well as the elimination of disilyl peroxide $[(t\text{-}Bu)_2HSiO\text{-}]_2$ (**10**). Compound **8** crystal data: monoclinic, $C2/c$, $a = 31.283$ (3) Å, $b = 8.350$ (1) Å, $c = 16.312$ (2) Å, $\beta = 126.63$ (1)°, $Z = 8$.

Introduction

The reductive coupling of metal-coordinated carbon monoxide is a current research objective, particularly with regard to the goal of CO conversion reactions (Fischer-Tropsch synthesis).[1] Key steps in the metal-mediated CO-coupling reaction are CO activation and reduction and subsequent CC coupling of the highly reactive carbyne units in the coordination sphere of a transition metal. Lippard has recently shown that the siloxycarbyne complex $[Ta({\equiv}COSiR_3)(CO)(dmpe)_2]$ (**2**) is a stable intermediate in the reduction of $[Ta(CO)_2(dmpe)_2Cl]$ (**1**) with Na/Hg in the presence of R_3SiCl to the acetylene complex $[Ta(R_3SiOC{\equiv}COSiR_3)(dmpe)_2Cl]$ (**3**).[2,3] A CO-bridged dinuclear tantalum siloxycarbyne complex **4** was also isolated from this reaction[4] (eq 1). Similar results have been

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[1] Vrtis, R. N.; Lippard, S. J. *Isr. J. Chem.* **1990**, *30*, 331.

[2] Vrtis, R. N.; Bott, S. G.; Rardin, L.; Lippard, S. J. *Organometallics* **1991**, *10*, 1364-1373.

[3] For η^2-ketenyl intermediates see ref 1.

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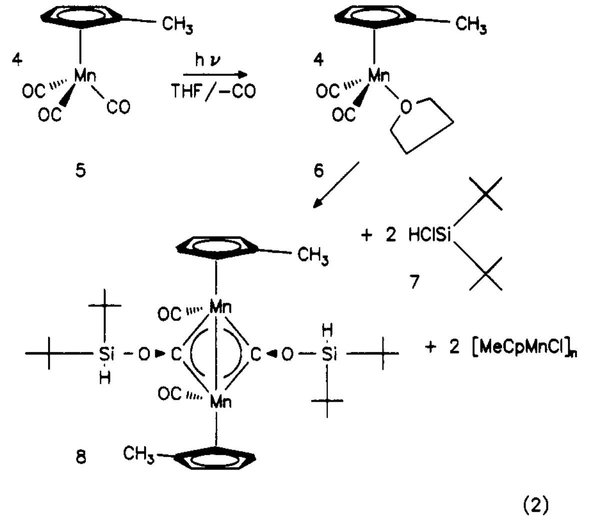
$$[Ta(CO)_2(dmpe)_2Cl] \xrightarrow[R_3SiCl]{Na/Hg}$$
$$\mathbf{1}$$
$$[Ta(\equiv COSiR_3)(CO)(dmpe)_2] \xrightarrow{R_3SiCl} [Ta(R_3SiOC\equiv COSiR_3)(dmpe)_2Cl]$$
$$\mathbf{2} \qquad\qquad\qquad\qquad \mathbf{3}$$
$$[(dmpe)_2(CO)Ta{=}C{=}O{-}Ta(Me_3SiOC\equiv COSiMe_3)(dmpe)_2] \quad (1)$$
$$\mathbf{4}$$

obtained by Chisholm for CC-coupling reactions of related tungsten complexes.[5] In these cases, however, the addition of stoichiometric amounts of a reducing agent (e.g. Mg or Zn) proved to be neccessary for the reduction of CO.[1]

In this paper we wish to report a new silane-induced CO activation process in the reaction of [(η^5-$H_3CC_5H_4$)Mn-(CO)$_2$·THF] (**6**) with (t-Bu)$_2$SiHCl (**7**)[6] for which a spontaneous reduction of the activated CO ligand by single electron transfer from the transition metal (formation of Mn(I) → Mn(II)) is observed. The cyclic bis(μ-carbyne) complex (η^5-$H_3CC_5H_4$)(CO)Mn(μ-COSiH(t-Bu)$_2$)$_2$Mn-(CO)(η^5-$H_3CC_5H_4$) (**8**) thus formed is the dimerization product of a highly reactive 17e$^-$ terminal siloxycarbyne complex [(η^5-$H_3CC_5H_4$)Mn(CO)≡COSiR$_3$] intermediate. As further consecutive reactions of **8**, a thermally induced CC-coupling reaction of both carbyne units to form the bis(siloxy)acetylene **9** as well as a 1,3-cis elimination of disilyl peroxide **10** from **8** have been observed as competing process.

Results and Discussion

Synthesis and Spectroscopic Properties of 8. The synthetic procedures applied utilize the photochemical generation of the solvent-stabilized 16e$^-$ species [(η^5-$H_3CC_5H_4$)Mn(CO)$_2$·THF] (**6**) by photolysis of (η^5-$H_3CC_5H_4$)Mn(CO)$_3$ (**5**). [(η^5-H_3CC_5H)Mn(CO)$_2$·THF] (**6**) has been isolated in 90% yield (3 h, quantum yield 3.3%) and subjected to a further "dark reaction"[7] with (t-Bu)$_2$SiHCl (**7**) which resulted in formation of the cyclic bis(μ-carbyne) complex **8** and [(η^5-$H_3CC_5H_4$)Mn^{II}Cl]$_n$ (eq 2). The bis(carbyne) complex **8** can be readily identified from its IR spectrum (ν_{CO} 1934, 1883 cm^{-1}). The high volatility of **8** allows the observation of a mass spectrum with the molecular ion at m/e 666 (5%). The ^{13}C NMR spectrum of **8** contains signals at 236.7 ppm for the coordinated CO ligand and 402.1 ppm for the μ-carbyne C atom. The observation of two bands for the ν_{CO} mode is indicative of the formation of the cis-isomer of **8**.



(2)

Table I. Product Distribution: Photoreaction of the 16e$^-$ Species [CpMn(CO)$_2$] with Various Silanes

silane	carbyne complex:silyl complex product ratio^c				yield (%)^d
(t-Bu)$_2$SiHCl^a	1	8	0		15
(t-Bu)$_2$SiHCl^b	1	8	traces	11	7
SiHCl$_3$^{a}	0.1	12	0.9	13	29
Ph$_2$SiH$_2$^{a}	0.1	14	0.9	15	7
Ph$_2$SiHCl^a	0.3	14	0.7	16	7

^{a} Reaction of the THF complex CpMn(CO)$_2$·THF (**6**). ^{b} Cophotolysis of **5** and silane in pentane. ^{c} Product distribution by ^{1}H NMR. ^{d} Overall yield with respect to **5**.

[(η^5-$H_3CC_5H_4$)MnCl]$_n$ forms an insoluble white precipitate in pentane which has been characterized by elemental analysis, IR spectroscopy, and measurement of its EPR spectrum (g = 2.001). Further reactions of **5**/**6** with the sterically less bulky silanes HSiCl$_3$, Ph$_2$SiHCl, and Ph$_2$SiH$_2$ give the thermolabile bis(μ-carbyne) complexes **12** and **14**, which have been spectroscopically characterized (Table I). In these cases, formation of the silyl hydrides **11**, **13**, **15**, and **16** as products of an oxidative addition at the 16e$^-$ complex generated from **6** (attack at Mn) becomes important. Modification of the geometry of the metal fragment has a strong influence on the product distribution: Introduction of the ethylpentamethylcyclopentadienyl substituent in (η^5-EtMe$_4$C$_5$)Mn(CO)$_3$ (**18**) and reaction of the photolytically generated species [(η^5-EtMe$_4$C$_5$)Mn-(CO)$_2$·THF] (**19**) with (t-Bu)$_2$SiHCl (**7**) yields the bis(μ-carbyne) complex **20**, but also the carbonyl complex **22** with a manganese–manganese triple bond (eq 3).[8] The formation of **22** is only observed in the presence of **7**, which obviously plays an important role in the CO activation process.

Solid-State Structure of 8. A single-crystal X-ray structure analysis of **8** (Figure 1) confirms the molecular constitution of the compound deduced by spectroscopic methods and shows further structural details. The molecule is dimeric with a Mn–C15 (μ-carbyne) bond length of 1.857 (2) Å and a Mn–Mn′ bond distance of 2.565 (1) Å; the latter one is typical for a Mn–Mn single bond.[9] The Mn–C15 (carbyne) bond is short compared to known Mn–C single bonds, for example that in (CO)$_4$MnC-(COOEt)C(HgBr)C(OEt)O is found to be 2.051 (26) Å.[9] For the acyclic carbine complex [Cp(CO)$_2$Mn≡C—CH=CPh$_2$]$^+$BF$_4^-$ the MnC distance is 1.665 (5) Å;[10] comparable

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(4) Vrtis, R. N.; Bott, S. G.; Lippard, S. J. *Organometallics* **1992**, *11*, 270–277.

(5) (a) Chacon, S. T.; Chisholm, M. H.; Cook, C. M.; Hampden-Smith, M. J.; Streib, W. E. *Angew. Chem.* **1992**, *104*, 476; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 462. (b) Bubro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311.

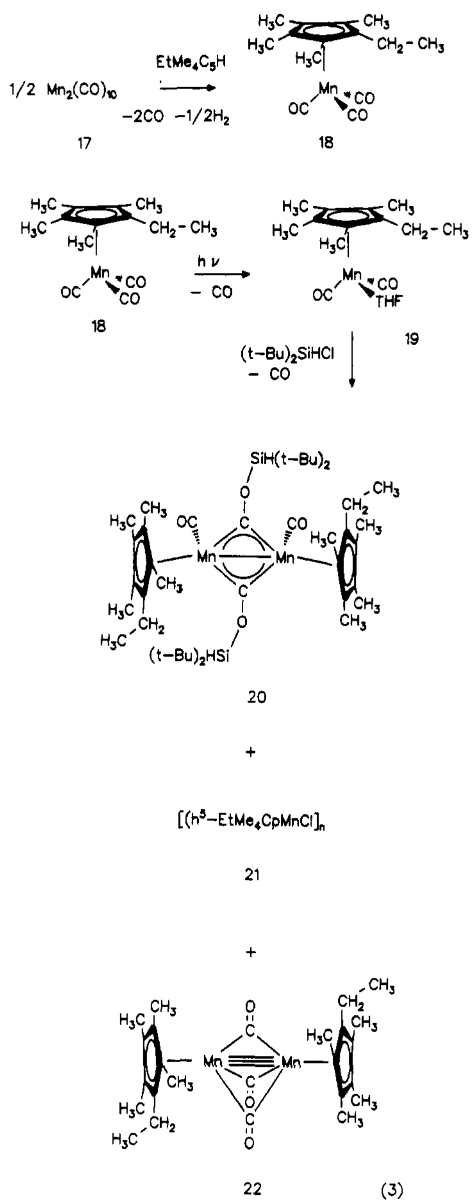
(6) Weidenbruch, M.; Peter, W. *Angew. Chem.* **1975**, *87*, 670; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 642.

(7) Karsch, H. H. *Habilitationsschrift*; Technische Universität München: Garching, FRG, 1969; p 1.

(8) Herrmann, W. A.; Serrano, R.; Weichmann, J. *J. Organomet. Chem.* **1983**, *246*, C57.

(9) (a) Herrmann, W. A. *Angew. Chem.* **1974**, *86*, 895; *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 861. (b) Herrmann, W. A.; Ziegler, M. L.; Serhadli, O. *Organometallics* **1983**, *2*, 958–962.

(10) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *262*, 39–47.



(3)

values for cyclic complexes of Mn are unknown. The coordination geometry at the C15 carbyne atom is trigonal planar with a bond angle Mn—C15—Mn′ of 87.2 (1)°. In contrast to known structures of related metallacycles, e.g. in $W_2(\mu\text{-}CSiMe_3)_2(O\text{-}i\text{-}Pr)_4$, the four-membered ring in 8 is folded along the Mn–Mn′ bond with an angle of 18.45° (Figure 2). Further bond distances and angles are given in Tables II–IV.

The two methylcyclopentadienyl substituents are located in cis positions; this cis-isomer is exclusively formed according to eq 2. Also, extended photolysis of *cis*-8 at 254 nm in methylcyclohexane or thermal treatment of 8 at 50 °C does not induce any isomerization process.[11-13] The cis-isomer features an all-trans position of the substituents at the ring as the sterically most favored arrangement.

Mechanism of Carbyne Complex Formation. A prerequisite for CO activation in 6 is an O attack of the silane at the coordinated carbonyl ligand. This activation step induces the reduction of CO by formal electron transfer Mn → C and yields a highly reactive 17e⁻ intermediate siloxycarbyne complex which dimerizes to give 8.

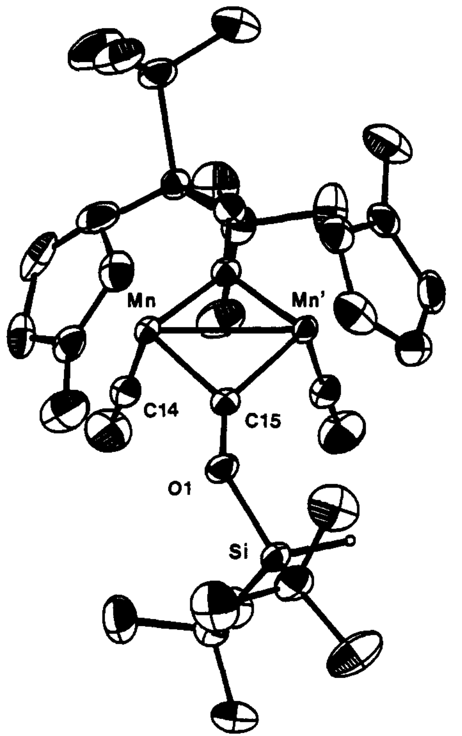


Figure 1. Molecular structure of $(\eta^5\text{-}H_3CC_5H_4)(CO)Mn(\mu\text{-}CO\text{-}SiH(t\text{-}Bu)_2)_2Mn(CO)(\eta^5\text{-}H_3CC_5H_4)$ (8) and the crystal numbering scheme used (ORTEP, displacement ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

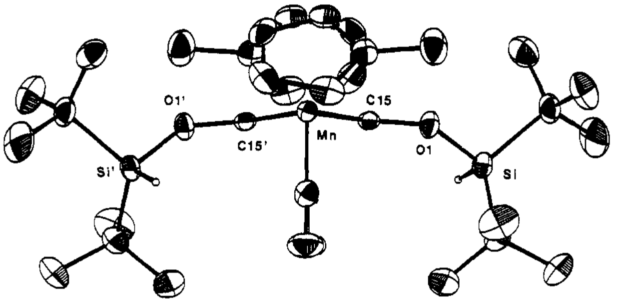
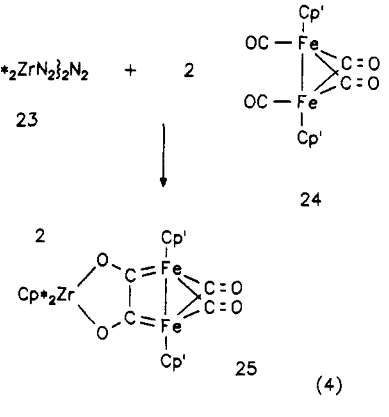


Figure 2. Side view of 8 showing the folding of the metallacycle.

Examples for a similar reaction pathway are well documented in the literature. Berry and Bercaw have reported CO activation in $Cp^*(OC)Fe(\mu\text{-}CO)_2Fe(CO)Cp^*$ (**24**) by $\{Cp^*{}_2ZrN_2\}_2N_2$ (**23**) and subsequent reductive CC coupling to form **25** (eq 4).[14] A particularly instructive example



(4)

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(11) Cotton, F. A.; Hanson, B. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; *Academic Press*: New York, 1980; p 379.

(12) An isomerization process is possible by the Cotton Adams mechanism and requires opening of the Mn–C15 bond. However, this process could not be observed.

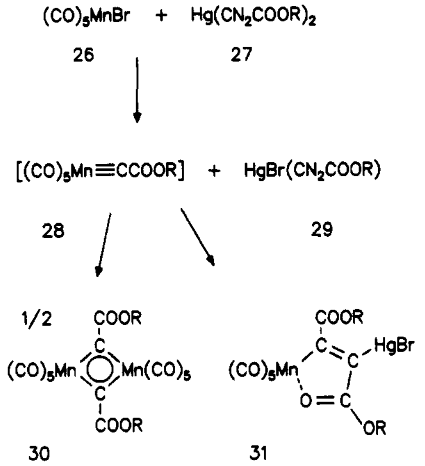
(13) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes; K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712.

Table II. Crystal Structure Data for 8

formula	$C_{32}H_{50}Mn_2O_4Si_2$
M_r (g/mol)	666.810
cryst dimens, mm	0.20 × 0.20 × 0.40
cryst syst	monoclinic
space group	$C2/c$ (No. 15)
a, Å	31.283 (3)
b, Å	8.350 (1)
c, Å	16.312 (2)
β, deg	126.63 (2)
V, Å^3	3419.40
Z	8
d_{calcd}, g/cm^3	1.56
μ(Mo Kα), cm^{-1}	8.0
$F(000)$, e	335
T, °C	−50
scan	ω
scan width (in θ), deg	0.8
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.5946
hkl range	+36, ±9, ±19
no. of rflns (measd/unique)	3298/3001
R_{int}	0.0268
no. of rflns obsd ($F_0 \geq 4.0\sigma(F_0)$)	2618
H atom (found/calcd)	50
no. of params refined	285
R^a	0.0280
$R_w{}^b$	0.0267
(shift/error)$_{max}$	0.001 p
$\Delta\rho_{fin}$(max/min), e/Å^3	+0.4354/−0.3722

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(F_o)$; function minimized $\sum_w(|F_o| - |F_c|)^2$.

with respect to the mechanism of the CC-coupling reaction stems from the work of Herrmann et al. (eq 5).[9] Reaction



(5)

of the carbonyl complex **26** with the mercury diazomethane **27** gives the highly reactive 17e⁻ intermediate carbyne complex **28** which dimerizes to form the bis(μ-carbyne) complex **30**. In this case, the intermediate carbyne complex **28** has been trapped by reaction with the mercury diazomethane **29** to form the cyclic vinylidene complex **31**. **31** was also characterized by a single-crystal X-ray structure analysis.

Further insight into the reaction mechanism of the CO activation process of eq 2 is provided by variation of the substituent pattern of the introduced silane (Table I): The yield of μ-carbyne complex (O attack of the silane) compared to silyl hydride formation (Mn attack of the silane) is a function of the Lewis acidity of the silane. However, even when the strongly acidic $HSiCl_3$ as reagent, the product ratio **12**:**13** is still 1:9.

Table III. Selected Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of 8[a]

Bond Distances			
Mn–C1	2.192 (2)	Mn–C2	2.181 (2)
Mn–C3	2.164 (2)	Mn–C4	2.145 (2)
Mn–C5	2.144 (2)	Mn–C14	1.775 (2)
Mn–C15	1.857 (2)	Mn–Mn′	2.565 (1)
C1–C1A	1.494 (3)	C1–C2	1.398 (3)
C1–C5	1.405 (3)	C2–C3	1.402 (3)
C3–C4	1.391 (4)	C4–C5	1.425 (4)
Si–C6	1.887 (2)	Si–C10	1.891 (2)
Si–O1	1.680 (1)	C6–C7	1.544 (3)
C6–C8	1.523 (4)	C6–C9	1.523 (4)
C10–C11	1.532 (3)	C10–C12	1.531 (3)
C10–C13	1.538 (3)	C14–O11	1.159 (3)
Bond Angles			
C1–Mn–C2	37.3 (1)	C1–Mn–C3	63.2 (1)
C2–Mn–C3	37.7 (1)	C1–Mn–C4	63.9 (1)
C2–Mn–C4	63.0 (1)	C3–Mn–C4	37.7 (1)
C1–Mn–C5	37.8 (1)	C2–Mn–C5	62.8 (1)
C3–Mn–C5	63.6 (1)	C4–Mn–C5	38.8 (1)
C1–Mn–C14	118.2 (1)	C2–Mn–C14	153.6 (1)
C3–Mn–C14	136.1 (1)	C4–Mn–C14	100.3 (1)
C5–Mn–C14	91.3 (1)	C1–Mn–C15	150.3 (1)
C2–Mn–C15	113.0 (1)	C3–Mn–C15	92.0 (1)
C4–Mn–C15	107.2 (1)	C5–Mn–C15	145.6 (1)
C14–Mn–C15	90.9 (1)	Mn–C15–Mn′	87.2 (1)
Mn–C1–C1A	128.6 (2)	Mn–C1–C2	70.9 (1)
C1A–C1–C2	126.6 (2)	Mn–C1–C5	69.3 (1)
C1A–C1–C5	126.2 (2)	C2–C1–C5	106.9 (2)
Mn–C2–C1	71.8 (1)	Mn–C2–C3	70.5 (1)
C1–C2–C3	109.2 (2)	Mn–C3–C2	71.8 (1)
Mn–C3–C4	70.4 (1)	C2–C3–C4	108.1 (2)
Mn–C4–C3	71.9 (1)	Mn–C4–C5	70.6 (1)
C3–C4–C5	107.4 (2)	Mn–C5–C1	72.9 (1)
Mn–C5–C4	70.6 (1)	C1–C5–C4	108.3 (2)
C6–Si–C10	118.8 (1)	C6–Si–O1	106.2 (1)
C10–Si–O1	104.6 (1)	Si–C6–C7	108.8 (2)
Si–C6–C8	112.8 (2)	C7–C6–C8	110.0 (2)
Si–C6–C9	108.0 (2)	C7–C6–C9	108.1 (2)
C8–C6–C9	109.1 (2)	Si–C10–C11	111.0 (2)
Si–C10–C12	106.7 (2)	C11–C10–C12	109.1 (2)
Si–C10–C13	112.8 (2)	C11–C10–C13	108.8 (2)
C10–C13–H133	112 (2)	H131–C13–H133	106 (2)
H132–C13–H133	107 (2)		

[a] Estimated standard deviations in units of the last significant *figure are given in parentheses.*

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 8

atom	x/a	y/b	z/c	U(eq),[a] Å^2
Mn	0.47717 (1)	0.21777 (3)	0.65353 (2)	0.017
C1	0.41085 (8)	0.3733 (3)	0.5416 (2)	0.034
C1A	0.3568 (1)	0.3865 (4)	0.5173 (3)	0.056
C2	0.45524 (9)	0.4681 (3)	0.6104 (2)	0.034
C3	0.49695 (9)	0.4279 (3)	0.6047 (2)	0.031
C4	0.4791 (1)	0.3070 (3)	0.5325 (2)	0.060
C5	0.4255 (1)	0.2718 (3)	0.4934 (2)	0.043
Si	0.37974 (2)	0.07763 (7)	0.76204 (4)	0.019
C6	0.33439 (9)	0.2212 (3)	0.7659 (2)	0.031
C7	0.3175 (2)	0.1447 (5)	0.8287 (3)	0.065
C8	0.2853 (1)	0.2660 (5)	0.6599 (2)	0.060
C9	0.3661 (1)	0.3722 (4)	0.8211 (3)	0.043
C10	0.35001 (8)	−0.1087 (3)	0.6806 (2)	0.022
C11	0.3225 (2)	−0.0699 (4)	0.5677 (2)	0.042
C12	0.3963 (1)	−0.2239 (3)	0.7175 (2)	0.036
C13	0.3098 (1)	−0.1926 (4)	0.6915 (2)	0.022
C14	0.47138 (8)	0.0092 (3)	0.6279 (1)	0.023
O11	0.46702 (7)	−0.1256 (2)	0.6072 (1)	0.036
O1	0.40507 (5)	0.1799 (2)	0.7113 (1)	0.023
C15	0.54733 (7)	0.1919 (2)	0.7674 (1)	0.016

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$.

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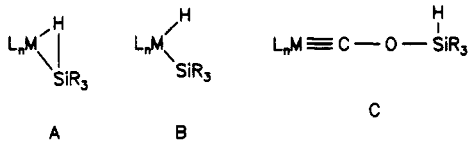
(14) Prolonged photolysis of **5** in N_2 atmosphere also gave formation of the N_2 complex $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2N_2$: (a) Sellmann, D.; Kleinschmitt, D. *Z. Naturforsch.* **1977**, *32B*, 795–801. (b) Sellmann, D. *Angew. Chem.* **1971**, *83*, 1017; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 919. (c) Ziegler, M. L.; Weidenhammer, K.; Zeiner, H.; Skell, P. S.; Herrmann, W. A. *Angew. Chem.* **1976**, *88*, 761; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 695.

Chart I



The stability of the carbyne complexes is strongly dependent upon the steric requirements of the silane used, and only the *tert*-butyl-substituted derivatives are stable for prolonged periods. Photolysis of **5** in a nonstabilizing hydrocarbon solvent gives lower yields of **8** and only traces of (η^5-$H_3CC_5H_4$)MnH$(CO)_2$SiH(*t*-Bu)$_2$ (**11**), which underlines a strong solvent influence.

Previous investigations of the photolysis reactions of **5** in the presence of various silanes only showed the products of Si–H activation.[15] Metal silyl hydride formation, however, becomes the main reaction path with sterically less hindered silanes.[16]

The insertion reaction of 16e$^-$ complexes into the Si–H bond has been investigated by Graham,[17] Schubert,[18] and Crabtree;[19] theoretical work on the insertion mechanism has been performed by Saillard[20] and Lichtenberger.[21] By variation of the Lewis basicity of the metal complex respectively with the Lewis acidity of the silane, different stages of the Si–H insertion reaction have been observed either with a side-on coordination of the Si–H (3c2e) bond and a μ-H bridge (A) or a conventional hydride structure (B) as ground-state geometry. For (η^5-$H_3CC_5H_4$)MnH$(CO)_2$SiHPh$_2$ (**15**) a structure (A) with a 3c2e μ-H bond has been proposed. The bond has been shown to be formed by a donor interaction of a σ-Si–H orbital with an empty d-orbital of the metal.[22]

In this paper, a further reaction channel involving CO activation by O attack of the silane (C) and subsequent carbyne complex formation by electron transfer Mn → C and dimerization of the formed 17e$^-$ intermediate to a stable bis(μ-carbyne) complex **8** is described (Chart I). This reaction mode sheds new light on the mechanism of the Si–H activation reaction of the 16e$^-$ complex [(η^5-$H_3CC_5H_4$)Mn$(CO)_2$·THF] (**6**).

Ligand-Coupling Reactions. CC-coupling reactions of carbyne ligands are of great interest and have been observed so far for a variety of acyclic, terminal bis(carbyne) complexes. In most cases, the complexes are generated at low temperatures as reactive intermediates. In this paper, evidence is provided for a coupling reaction of two carbyne units in a cyclic system. An important factor for this CC-coupling reaction is the folding of the metallacycle **8**, which has not been observed in related systems e.g. $W_2(\mu$-CSiMe$_3)_2$(O-*i*-Pr)$_4$. The observed ring geometry in **8** allows the two carbyne C atoms to come into proximity (nonbonding distance C15–C15′ of 2.662 (2) Å) which opens up a reaction channel for transannular CC-coupling reactions. Indeed, a thermolysis reaction of **8** gives the bis(siloxy)acetylene **9** as the product of a CC bond formation reaction between the two carbyne units: Thermogravimetric investigations of **8** in a He gas flow coupled with quadrupole mass spectroscopy in the temperature range from 78 (onset) to 200 °C give evidence for the formation of bis(di-*tert*-butylsiloxy)acetylene (**9**) in ca. 21% yield and bis(di-*tert*-butylsilyl) peroxide (**10**) in 79% yield (Figure 3).[23]

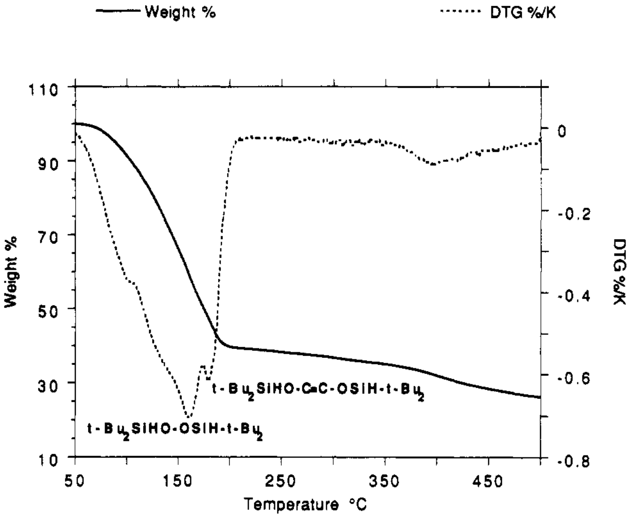
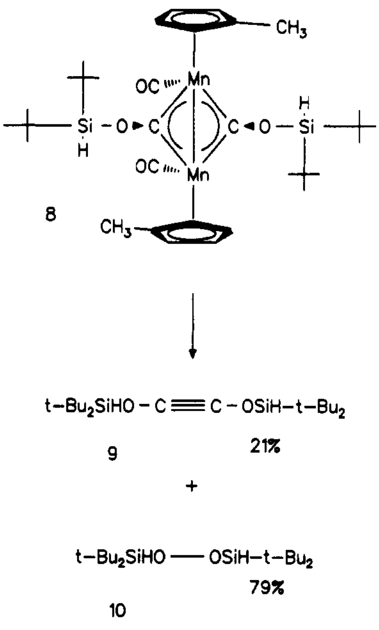


Figure 3. Thermogravimetric analysis of **8**. See text for details.

Pyrolysis of **8** at 180 °C/10^{-4} Torr also results in bis(siloxy)acetylene **9** (1.7%) formation as well as 1,3-cis elimination of the silyl peroxide (3.3%) **10** as a competing processes. Furthermore, (η^5-$H_3CC_5H_4$)Mn$(CO)_3$ (**5**) (39.4%), $H_3CC_5H_3$SiH(*t*-Bu)$_2$ (18.8%) (**32**) and (*t*-Bu)$_2$O (36.9%) (**33**) are observed (eq 6).



(6)

Experimental Section

All experiments have been performed under an atmosphere of dry argon; air-sensitive materials were handled by standard Schlenk techniques. The solvents were dried by distillation from NaK alloy or P_4O_{10}. Residual water content was determined by Karl Fischer titration and was generally below 3.5 ppm. The preparation of di-*tert*-butylchlorosilane has been described in the

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(17) Hart-Davies, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* **1971**, *93*, 4388.

(18) Schubert, U.; Müller, J.; Alt, H. G. *Organometallics* **1987**, *6*, 469.

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(20) Rabaa, H.; Saillard, J. Y.; Schubert, U. *J. Organomet. Chem.* **1987**, *330*, 397.

(21) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1989**, *111*, 3538.

(22) Lichtenberger, D. L.; Rai-Chaudhuri, A. *J. Am. Chem. Soc.* **1990**, *112*, 2492–2497.

(23) Analysis of the residue (38% Mn) did not reveal any definitive compounds.

literature;[6] all other chemicals were commerically available.

Spectra. IR spectra were recorded on a Nicolet FT 5DX instrument as KBr pellets, a Nujol suspension, or a solution in 0.1 mm KBr cells. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a JEOL GX 400 spectrometer at 400.01, 53.5, and 36.0 MHz and a JEOL FX 270 instrument at 270.1 MHz (^1H). ^{29}Si NMR spectra were partially recorded with DEPT and INEPT pulse programs. ^1H and ^{13}C chemical shifts were measured using the solvent references as standard; ^{29}Si chemical shifts were referenced to external Me_4Si in the same solvent.

UV irradiation was performed in a quartz apparatus with a 150-W Hg high-pressure immersion lamp with a flux of 15 W (254 nm), which corresponds to 0.115 (mol equiv)/h. The reactions had quantum yields of approximately 3–4%.

TG–MS analysis was done on a Perkin-Elmer TGA 7 instrument with a heating rate of 5 °C min^{-1} in a dynamic He atmosphere coupled with a QMG 420 mass spectrometer (Balzers); EPR spectra were measured on a Jeol JES RE2X spectrometer at room temperature.

Microanalyses were carried out at Mikroanalytisches Laboratorium der Technischen Universität München by Ms. U. Graf and M. Barth.

$(\eta^5\text{-}H_3CC_5H_4)(CO)\overline{Mn(\mu\text{-}COSiH(t\text{-}Bu)_2)_2Mn}(CO)(\eta^5\text{-}H_3CC_5H_4)$ (8), Bis[carbonyl(μ-di-*tert*-butylsiloxycarbyne)(η^5-methylcyclopentadienyl)manganese]. A solution of 2.0 g (12.7 mmol) of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ in 270 mL of THF was photolyzed for 3 h at −60 °C in a quartz apparatus equipped with a 150-W Hg high-pressure immersion lamp. The mixture was allowed to warm to room temperature and the solvent removed in high vacuum. The residue contained crude 6 which was purified by washing with pentane. 6 was dissolved again in 150 mL of THF, the solution was cooled to −70 °C, and 5.0 mL (24.7 mmol) of $HClSi(t\text{-}Bu)_2$ was added. The mixture was allowed to warm to room temperature and stirred for an additional 10 h until the ν_{CO} bands of $[(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2\cdot THF]$ had disappeared and the formation of 8 (IR: ν_{CO} 1924, 1871 cm^{-1}) was completed. Photolytic reactions were also monitored by volumetric measurement of the evolved CO.

After removal of the THF in vacuum, 8 was separated from the Mn(II) product by filtration. The solvent (and any residual $(t\text{-}Bu)_2SiHCl$ and $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$) was removed in high vacuum (5×10^{-5} bar). 8 was crystallized from pentane at −78 °C in 15% yield (referenced to $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (**5**)); mp 181 °C dec.

8: ^1H NMR (270 MHz, $CDCl_3$, 22 °C, TMS) δ 1.20 (s, 18 H, *t-Bu*), 2.15 (s, 3 H, CH_3), 3.90, 4.70 (m, 4 H, *Cp*), 4.95 (s, 1 H, Si*H*); ^{13}C NMR (67.8 MHz, $CDCl_3$, 23 °C) δ 14.4 (q, $^1J(^1H^{13}C) = 130.6$ Hz, CH_3), 19.9 (s, *t-Bu*), 27.4 (q, $^1J(^1H^{13}C) = 127.0$ Hz, *t-Bu*), 86.6 (d, $^1J(^1H^{13}C) = 176.8$ Hz), 87.8 (d, $^1J(^1H^{13}C) = 168.5$ Hz, *Cp*), 101.9 (s, Me*Cp*), 236.7 (s, *CO*), 402.1 (s, μ-*C*); ^{29}Si NMR (53.3 MHz, $CDCl_3$, 22 °C) δ 19.7 (m, $^1J(^1H^{29}Si) = 205.9$ Hz, $^3J(^1H^{29}Si) = 6.3$ Hz). IR (cm^{-1}, pentane): 1934 (s), 1883 (s) (ν_{CO}). MS (EI, 70 eV; *m/e* (relative intensity)) 666 (M^+, 5%, correct isotope distribution). Anal. Calcd for $C_{32}H_{22}O_4Mn_2Si_2$ (M_r 666.81 g/mol): C, 57.84; H 7.86. Found: C, 56.91; H, 7.75. $[(\eta^5\text{-}H_3CC_5H_4)MnCl]_n$ EPR (THF): $g = 2.001$. Anal. Calcd for $C_8H_{16}Cl_2MnO_2$ (M_r 270.06 g/mol): C, 35.58; H, 5.97; Cl, 26.26. Found: C, 36.12; H, 5.99; Cl, 26.21.

X-ray Structure Determination of 8. A suitable single crystal of 8 was grown from a pentane solution at −78 °C. The crystal was sealed into a glass capillary under argon at dry ice temperature. A summary of the crystal data and important numbers pertinent to data collection and structure refinement is given in Table II. The integrated intensities were collected on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å, scan speed (in θ) 0.7–29.3°/min). Repeated measurement of three standard reflections did not indicate significant crystal decay or misalignment during data collection. No correction for absorption or L_p effects was applied. The structure of 8 was solved by direct methods and completed by Fourier techniques. The non-hydrogen atoms were refined with anisotropic displacement parameters in one large block. All hydrogen atoms were found and refined isotropically. Atomic form factors for neutral, isolated atoms were those of Cromer and Waber;[24] those for hydrogen were based on the bonded, spherical model of Stewart, Davidson, and Simpson.[25] The programs used included SHELXS-86[26] (structure solution), SHELX-76[27] (refinement), and ORTEP[28] (molecular drawings), as well as locally written routines. Tables III and IV contain the bond distances and angles and atomic coordinates with equivalent isotropic displacement parameters; Figures 1 and 2 show the molecular structure of 8 and the crystallographic numbering scheme adopted. Further data for the structure determination are available as supplementary material.

Cophotolysis of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (5) and $(t\text{-}Bu)_2SiHCl$ (7) in Pentane. A 3.15-mL (20.0-mmol) sample of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (**5**) and 40.0 mL (198 mmol of $HClSi(t\text{-}Bu)_2$ (**7**) were dissolved in 200 mL of pentane and photolyzed (high-pressure Hg immersion lamp, 150 W, quartz apparatus) for 3 h at −70 °C. The resulting yellow mixture was allowed to warm to room temperature which resulted in intensification of the color of the solution. The mixture was concentrated to 20 mL in vacuum and worked up as described for 8. Spectroscopic investigations showed the formation of 8 in 7% yield besides traces (0.1%) of $(\eta^5\text{-}H_3CC_5H_4)MnH(CO)_2SiCl(t\text{-}Bu)_2$ (**11**). Prolonged photolysis under N_2 yielded the N_2 complex $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2N_2$: IR ($cm^{-1}$, THF) 2165 ($\nu_{NN}$), 1980, 1923 ($\nu_{CO}$).[14]

$(\eta^5\text{-}H_3CC_5H_4)MnH(CO)_2SiCl(t\text{-}Bu)_2$ (11), (Chloro-di-*tert*-butylsilyl)dicarbonylhydrido(η^5-methylcyclopentadienyl)manganese. ^1H NMR (270 MHz, C_6D_6, 22 °C, TMS): δ −11.3 (s, 1 H, Mn–*H*), 1.15 (s, 18 H, *t-Bu*), 1.50 (s, 3 H, CH_3), 4.0 (s, 4 H, *Cp*). IR (cm^{-1}, THF): 1987 (s), 1928 (s) (ν_{CO}). Anal. Calcd for $C_{16}H_{26}ClMnO_2Si$ (M_r 368.86 g/mol): C, 52.10; H, 7.11. Found: C, 51.31; H, 7.09.

Reaction of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2\cdot THF$ (6) with $HSiCl_3$. A 2.0-mL (12.7-mmol) sample of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (**5**) was photolyzed at −78 °C for 3 h until **5** was converted in ca. 90% yield to **6**. Then 1.3 mL (12.7 mmol) of $HSiCl_3$ in 10 mL of THF was added, and the reaction mixture was stirred for an additional 2 h at room temperature. All volatile components were removed in vacuum, and the mixture was worked up as described for 8. The μ-bis(carbyne) complex **12** was identified spectroscopically; however, attempts to isolate **12** were not successful due to the lability of the compound. The spectroscopically determined yield of **12** in the crude reaction mixture was 2.9%. $(\eta^5\text{-}H_3CC_5H_4)(CO)\overline{Mn(\mu\text{-}COSiHCl_2)_2Mn}(CO)(\eta^5\text{-}H_3CC_5H_4)$ (**12**): ^1H NMR (C_6D_6, 270 MHz, 22 °C) δ 2.20 (s, 3 H, CH_3), 4.0, 4.75 (4 H, *Cp*), 6.1 (s, 1 H, Si*H*); IR (THF) 1930 (s), 1875 (s) (ν_{CO}).

$(\eta^5\text{-}H_3CC_5H_4)MnH(CO)_2SiCl_3$ (**13**) was crystallized from the mother liquor of **12** in 26.1% yield in the form of yellow crystals; mp 112 °C. ^1H NMR (C_6D_6, 270 MHz, 22 °C): δ −10.4 (s, 1 H, Mn*H*), 1.55 (s, 3 H, CH_3), 3.95 (s, 4 H, *Cp*). IR (cm^{-1}, THF): 2017 (s), 1965 (s) (ν_{CO}). Anal. Calcd for $C_8H_8MnCl_3O_2Si$ (M_r 325.53 g/mol): C, 29.52; H, 2.48; Cl, 32.67. Found: C, 28.91; H, 33.01.

Reaction of 6 with Ph_2SiHCl and Ph_2SiH_2. A 5.0-mL (16.6-mmol) sample of $(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_3$ (**5**) in 250 mL of THF was photolyzed at −60 °C for 3 h until 90% conversion of **5** to **6** was achieved. The 1.5 mL (7.6 mmol) of $HClSiPh_2$ was added, and the mixture was worked up as described for 8. The μ-bis(carbyne) complex $(\eta^5\text{-}H_3CC_5H_4)(CO)\overline{Mn(\mu\text{-}COSiHPh_2)_2Mn}(CO)(\eta^5\text{-}H_3CC_5H_4)$ (**14**) could not be isolated in pure form due to its thermal instability; 2.1% yield (spectroscopically determined). $(\eta^5\text{-}H_3CC_5H_4)(CO)\overline{Mn(\mu\text{-}COSiHPh_2)_2Mn}(CO)(\eta^5\text{-}H_3CC_5H_4)$ (**14**): ^1H NMR (C_6D_6, 22 °C) δ 2.15 (s, 3 H, CH_3), 3.90, 4.70 (m, 4 H, *Cp*) 6.1 (s, 1 H, Si*H*), 7.2–7.8 (m, 10 H, C_6H_5); IR (cm^{-1}, THF) 1888 (s), 1933 (s) (ν_{CO}).

The mother liquor of **14** contained *cis*-$(\eta^5\text{-}H_3CC_5H_4)Mn(CO)_2HSiClPh_2$ (**16**) in 4.9% yield. ^1H NMR (C_6D_6, 22 °C): δ −11.6 (s, 1 H, Mn*H*), 1.33 (s, 3 H, CH_3), 3.90 (s, 4 H, *Cp*), 7.2–7.8

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(25) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(26) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985.

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(28) Johnson, C. K. ORTEP-II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(m, 10 H, C_6H_5). IR (cm^{-1}, THF): 1987 (s), 1930 (s) (ν_{CO}).[14] Anal. Calcd for $C_{20}H_{18}ClMnO_2Si$ (M_r 408.84 g/mol): C, 58.76; H, 4.44; Cl, 8.67. Found: C, 59.01; H, 4.54; Cl, 8.58.

During prolonged photolysis, also traces of *trans*-(η^5-$H_3CC_5H_4$)$Mn(CO)_2HSiClPh_2$ appeared as a secondary product of the photochemical rearrangement of the cis-isomer. ^{1}H NMR (C_6D_6, 22 °C): δ −11.5 (s, 1 H, Mn*H*), 1.32 (s, 3 H, CH_3), 3.89 (s, 4 H, *Cp*), 7.2–7.8 (m, 10 H, C_6H_5). IR (cm^{-1}, THF): 1953 (s) (ν_{CO}).

In the case of the reaction of **5**/**6** with Ph_2SiH_2, the reaction mixture of (η^5-$H_3CC_5H_4$)(CO)$\overline{\mathrm{Mn}(\mu\text{-COSiHPh}_2)_2\mathrm{Mn}}$(CO)($\eta^5$-$H_3CC_5H_4$) (0.7% yield) (**14**) and (η^5-$H_3CC_5H_4$)$Mn(CO)_2HSiHPh_2$ (6.3% yield) (**15**) was subjected to column chromatography (silica gel, column of 40-cm height and 2-cm diameter, −20 °C) which allowed isolation of **15**. (η^5-$H_3CC_5H_4$)$MnH(CO)_2SiHPh_2$ (**16**): ^{1}H NMR (C_6D_6, 22 °C) δ −11.0 (s, 1 H, Mn*H*), 1.5 (s, 3 H, CH_3), 4.0 (s, 4 H, *Cp*), 7.3–7.9 (m, 10 H, C_6H_5).[14] Anal. Calcd for $C_{20}H_{19}MnO_2Si$ (M_r 374.394 g/mol): C, 64.34; H, 4.86. Found: C, 65.12; H, 4.90.

TG–MS Analysis of 8. A sample of 3.754 mg of **8** was heated on a thermobalance TGA 7 (Perkin-Elmer) in a dynamic He atmosphere. The instrument was coupled to a QMG 420 quadrupole mass spectrometer (Balzers). A temperature program was applied with a heating rate of 5 deg min^{-1}. In the temperature range from 78 (onset) to 200 °C, formation of bis(di-*tert*-butyl)silyl peroxide (heating time 22.0 min, 79% overall yield, *m*/*e* = 318 (2%, M$^+$)) and bis(di-*tert*-butylsiloxy)ethyne (heating time 26 min, 21% overall yield, *m*/*e* = 342 (5%, M$^+$) as well as CO formation were observed (80 °C).

Pyrolysis of 8. A 1.3-g sample of **8** was heated to 180 °C at 10^{-4} Torr for 3 h. The volatile products were condensed at −196 °C onto a cooling finger. The condensate was separated into its components by either GC–MS or preparative GC. The following products were obtained. MS (EI, 70 eV, *m*/*e* (relative intensity)): $CpMn(CO)_3$ (39.4% yield), 218 (M$^+$, 3%); MeCpSiH(*t*-Bu)$_2$ (18.8%), 222 (M$^+$, 2%); (*t*-$Bu_2HSi)_2O$ (36.9%), 302 (M$^+$, 3%); (*t*-Bu_2HSi–O–)$_2$ (3.3%), 318 (M$^+$, 2%); (*t*-$Bu_2HSiOC{\equiv})_2$ (1.7%), 342 (M$^+$, 4%).

(η^5-EtMe$_4$C$_5$)Mn(CO)$_3$ (18), (η^5-Ethyltetramethylcyclopentadienyl)manganese Tricarbonyl. A 2.70-g (6.92-mmol) sample of $Mn_2(CO)_{10}$ and 10 mL of $EtMe_4C_5H$ were heated to 180 °C for 25 h. The formed brown mixture was cooled to room temperature, and all volatile components were removed in a high vacuum. The product was subjected to column chromatography on silica gel and eluted with pentane. **18** was isolated in the second intense yellow fraction (the first, slightly yellow fraction contained only impurities). **18** formed bright yellow crystals from pentane at −78 °C in 56% yield (2.23 g, 7.74 mol). ^{1}H NMR (C_6D_6, 21 °C): δ 0.75 (tr, 3 H, CH_3CH_2), 1.51–1.55 (m, 12 H, C_5Me_4), 2.00 (q, 2 H, CH_3CH_2). ^{13}C NMR (C_6D_6, 23 °C): δ 9.7 (q, CH_3, $^1J(^1H^{13}C)$ = 127 Hz), 9.9 (q, $^1J(^1H^{13}C)$ = 127 Hz, CH_3), 15.3 (q × tr, $^1J(^1H^{13}C)$ = 127 Hz, $^2J(^1H^{13}C)$ = 4.8 Hz, CH_3), 18.7 (tr × q, $^1J(^1H^{13}C)$ = 128 Hz, $^2J(^1H^{13}C)$ = 4.2 Hz, CH_2), 95.6, 100.7 (s, *Cp*), 227 (s, *CO*). IR (cm^{-1}, pentane): 2009 (s) 1927 (s) (ν_{CO}).[8]

Photolysis of (η^5-EtMe$_4$C$_5$)Mn(CO)$_3$ (18) and Reaction with (*t*-Bu)$_2$SiHCl. A 0.60-g (2.08-mmol) sample of (η^5-$EtMe_4C_5$)-$Mn(CO)_3$ (**18**) dissolved in 270 mL of THF was photolyzed for 30 min with a high-pressure Hg immersion lamp, and 2.10 mL (10.4 mmol) of (*t*-Bu)$_2$SiHCl at −40 °C was added. The formed red solution was stirred for an additional 3 h and allowed to warm to room temperature. All volatile components were removed in vacuum (5 × 10^{-2} bar); the residue was dissolved in pentane and separated from precipitated [(η^5-$EtMe_4C_5$)MnCl]$_n$ (**21**) by filtration. **20** crystallized as red needles from pentane. Yield 8%; mp 134 °C. ^{1}H NMR (C_6D_6, 22 °C): δ 0.95 (tr, 3 H, $^3J(^1H^1H)$ = 7.2 Hz, CH_3CH_2), 1.21 (s, 18 H, *t*-Bu), 1.60, 1.95 (s, 12 H, C_5Me_4), 2.50 (q, 2 H, $^3J(^1H^1H)$ = 7.2 Hz, CH_3CH_2), 4.92 (s, 1 H, Si*H*). IR (cm^{-1}, THF): 1889 (s), 1934 (s), (ν_{CO}). Anal. Calcd for $C_{42}H_{72}Mn_2O_4Si_2$ (M_r 807.08 g/mol): C, 62.50; H, 8.99. Found: C, 62.31; H, 8.91.

(η^5-EtMe$_4$C$_5$)Mn(μ-CO)$_3$Mn(η^5-EtMe$_4$C$_5$) (22), Bis(η^5-Ethyltetramethylcyclopentadienyl)tris(μ-carbonyl)dimanganese. (η^5-$EtMe_4C_5)_2Mn_2(CO)_3$ (**22**) was isolated from the reaction mixture of **18** described above by column chromatography on silica gel/pentane in 7% yield as dark green crystals. Mp: 152 °C. ^{1}H NMR (C_6D_6, 22 °C): δ 1.55 (s, br, 3 H, CH_3CH_2), 1.65 (s, 12 H, CH_3), 2.05 (s, br, 2 H, CH_2). ^{13}C NMR (C_6D_6, 23 °C): δ 9.2 (q, $^1J(^1H^{13}C)$ = 127 Hz, CH_3), 9.4 (q, $^1J(^1H^{13}C)$ = 127 Hz, CH_3), 14.7 (q × tr, $^1J(^1H^{13}C)$ = 127 Hz, $^2J(^1H^{13}C)$ = 4.7 Hz, CH_3), 18.1 (tr × q, $^1J(^1H^{13}C)$ = 128 Hz, $^2J(^1H^{13}C)$ = 4.3 Hz, CH_2), 91.8, 95.3 (s, C_5Me_4Et), 271.0 (s, μ-*CO*). IR (cm^{-1}, pentane): 1782 ($\nu_{\mu CO}$). Anal. Calcd for $C_{25}H_{34}O_3Mn_2$ (M_r 492.42 g/mol): C, 60.98; H, 6.96. Found: 61.02; H, 6.96.

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Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic displacement parameters and bond distances and angles for 4 (3 pages). Ordering information is given on any current masthead page.

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