ORGANOMETALLICS

Preparation of a mixed-metal ketenylidene complex from Mn(CO)5(CX3) (X = Cl, Br)

Ann M. Crespi, and Duward F. Shriver

Organometallics, **1986**, 5 (8), 1750-1752• DOI: 10.1021/om00139a041 • Publication Date (Web): 01 May 2002

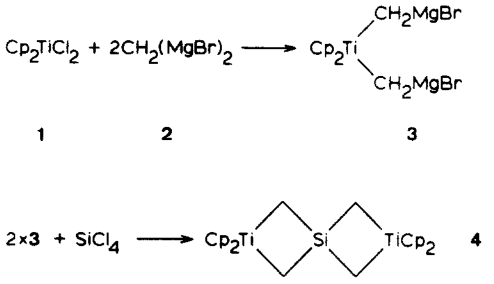
Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Table I. Spectroscopic Data of 4 and 5

	^{1}H NMR[a]			^{13}C NMR[b]				
compd	Cp	CH_2	CH_3	Cp	CH_2	CH_3	^{29}Si NMR[c]	UV
4	5.71	2.55	...	109.9 (d, 173)	70.9 (t, 131)	...	−145.3 (n, 5.6)	528
5	5.57	2.51	0.13	110.1 (d, 173)	70.6 (t, 130)	0.97 (q, 119)	−76[e]	478

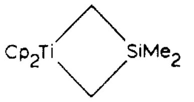
[a] δ in ppm; 90 MHz; C_6D_6 (C_6HD_5 at 7.17 ppm as internal standard); integrals in agreement with number of protons. [b] δ in ppm (multiplicity, ^1J(CH) in Hz); 62.89 MHz; C_6D_6 (at 128.0 ppm as internal standard). [c] δ in ppm (multiplicity (n = nonet), ^2J(SiH) in Hz); 79.48 MHz; C_6D_6 (Me_4Si as external standard). [d] λ_{max} in nm. [e] ^2J(Si–CH$_2$) = 4.9 Hz and ^2J(Si–CH$_3$) = 6.7 Hz determined from ^{29}Si satellites in the ^{1}H NMR spectrum.

Scheme I



chloride (0.35 mmol) was added. The reaction mixture was then warmed to room temperature whereupon the red precipitate dissolved. After 4 h, the solvent was evaporated to dryness and the residue extracted with benzene followed by filtration. The filtrate was evaporated to dryness and gave purple-red crystals of 4 (48% yield), which are only slightly sensitive to oxygen and moisture and can be sublimed (150 °C; 10^{-6} mbar). Compound 4 was identified by elemental analysis[3] and by its spectral properties (Table I).

To our surprise and initial discomfort, the ^{1}H and ^{13}C NMR data were very close to those of the monocyclic model 5;[2a,4] the structure of 5 had been confirmed by X-ray crystallography.[4] Reassuring differences, however, were found in the ^{29}Si NMR and UV spectra. The latter reveal a bathochromic shift for 4 relative to 5, indicating a smaller HOMO–LUMO gap in 4. On the one hand, it is tempting to ascribe this to ground-state destabilization due to rehybridization at silicon;[5] the well-known strain effect of spiro-annelation could be invoked.[6] On the other hand, ring strain is usually associated with downfield shifts of ^{29}Si.[7,8] This is well-illustrated by the "carbon analogues" of 4 and 5, i.e., 6 (δ(^{29}Si) 37.2) and 7 (δ(^{29}Si) 18.4),[7] respectively; relative to tetramethylsilane, 6 and 7 show a downfield shift which is nearly additive per four-membered ring.



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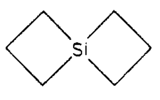

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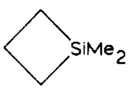

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An analogous additivity is observed for 4 and 5, but its direction is opposite and the increments are much larger (Table I). The cause for this dramatic upfield shift is not yet clear. Transannular bonding has been suggested to explain the downfield shift in 6 and 7. In view of the short Ti–Si distance in 5 (*d* = 2.786 Å;[9] cf. the sum of radii *r*(Ti) + *r*(Si) = 2.5 Å[10]) a direct interaction in 4 and 5 seems not impossible; anisotropic shielding by the Cp_2Ti unit[11] is another possibility. In this context and in view of the thermal stability of 4 and 5, it is also relevant to point out that the endocyclic angle strain at silicon in 5 (CH_2SiCH_2 = 101.3°)[4] is much smaller than in 7 (CH_2SiCH_2 = 80.6°).[12]

Compound 4 has been characterized chemically by reaction with iodine to give tetrakis(iodomethyl)silane (32% yield) and with trimethyltin chloride to give tetrakis[(trimethylstannyl)methyl]silane; both are new compounds and were characterized by their spectral properties.[13]

$$\mathrm{Si(CH_2I)_4} \xleftarrow{\mathrm{I_2}} 4 \xrightarrow{\mathrm{Me_3SnCl}} \mathrm{Si(CH_2SnMe_3)_4}$$

Acknowledgment. We thank Dr. F. J. J. de Kanter for measuring the ^{29}Si NMR spectra and Mr. A. F. Hamminga, University of Groningen, for the elemental analysis.

Registry No. 1, 1271-19-8; 2, 27329-47-1; 3, 96242-28-3; 4, 103259-05-8; $SiCl_4$, 10026-04-7; $Si(CH_2I)_4$, 103259-03-6; Me_3SnCl, 1066-45-1; $Si(CH_2SnMe_3)_4$, 103259-04-7.

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(3) Anal. Calcd for $C_{24}H_{28}SiTi_2$: C, 65.46; H, 6.41. Found: C, 64.77; H, 6.15.

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(13) $Si(CH_2I)_4$: ^{1}H NMR ($CDCl_3$; 90 MHz) δ 2.44 (s, 8 H); MS, *m/e* (relative intensity) 465 (100, $[M - I]^+$), 451 (5.9), 437 (3.6), 423 (15.2), 409 (18, SiI_3^+), 339 (3.3). $Si(CH_2SnMe_3)_4$: ^{1}H NMR (C_6D_6; 90 MHz) δ 0.30 (s, 36 H), 0.10 (s, 8 H).

Preparation of a Mixed-Metal Ketenylidene Complex from $Mn(CO)_5(CX_3)$ (X = Cl, Br)

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Received March 6, 1986

Summary: The reaction of $Mn(CO)_5(CBr_3)$ and [PPN]-[$Co(CO)_4$] yields the mixed-metal ketenylidene complex [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$]. The structure of the ketenylidene complex was determined by X-ray crystallography.

Numerous transition-metal cluster carbide complexes have been prepared by reactions between CCl_4 or $CHCl_3$

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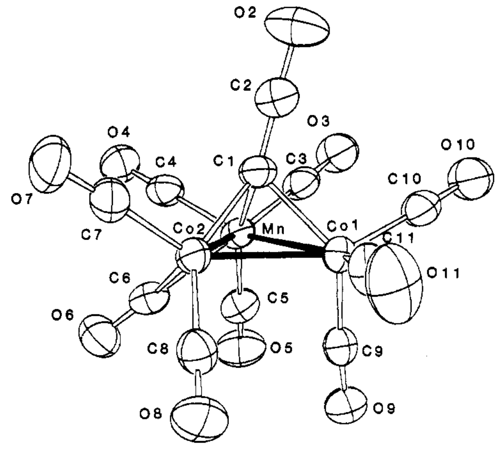


Figure 1. An ORTEP drawing of $MnCo_2(CO)_9(\mu_3\text{-}CCO)^-$. Some selected bond distances (Å) and angles (deg): Co1–Co2 = 2.480 (1); Co1–Mn = 2.643 (1); Co2–Mn = 2.568 (1); Co1–C1 = 1.968 (3); Co2–C1 = 1.914 (3); Mn–C1 = 2.002 (3); C1–C2 = 1.281 (4); C2–O2 = 1.173 (3); C1–C2–O2 = 177.7 (3).

and anionic metal carbonyl species of Co, Rh, and Ni.[1-4] The polyhalomethane is the source of the carbide atoms in these reactions. The present research is based on the idea that metal-substituted trihalomethanes might be useful reagents for building mixed-metal carbide clusters. Trihalomethyl transition-metal complexes are readily available from the halogen-exchange reaction between trifluoromethyl compounds and boron trihalides (eq 1).[5]

$$M\text{-}CF_3 + BX_3 \rightarrow M\text{-}CX_3 + BF_3 \qquad (1)$$

$$M = Mn(CO)_5,\ CpFe(CO)_2,\ CpMo(CO)_3;\ X = Cl,\ Br$$

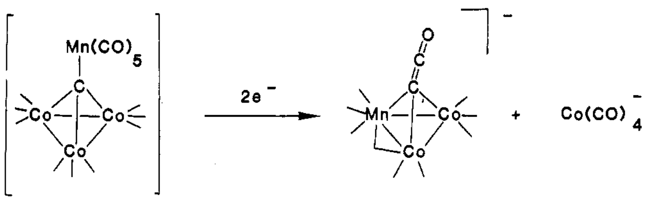
Our objective has been met by the formation of a trimetallic ketenylidene complex containing a carbide-like carbon atom from the reaction of $Mn(CO)_5(CX_3)$ and $[PPN][Co(CO)_4]$ (PPN = bis(triphenylphosphine)nitrogen(1+)).

The ketenylidene complex 1 is prepared by combining a 1:1.7 ratio of $Mn(CO)_5(CBr_3)$ and $[PPN][Co(CO)_4]$ in CH_2Cl_2 at −78 °C (eq 2). The solution turns dark brown

$$Mn(CO)_5(CBr_3) + [PPN][Co(CO)_4] \rightarrow [PPN][MnCo_2(CO)_9(\mu_3\text{-}CCO)] + \cdots \qquad (2)$$

as it is slowly warmed to room temperature. After extraction with hexane to remove the $Mn(CO)_5X$ that forms, the product 1 is extracted into diethyl ether. Several recrystallizations by slow diffusion of pentane into diethyl ether yield a dark brown crystalline product in 20% yield based on Co. The product was characterized by IR, ^{13}C NMR, and X-ray crystallography.[6,7]

Scheme I



The Mn–Co and Co–Co bond distances compare favorably with those found in the literature.[8-11] The carbonyl ligands are unsymmetrically disposed around the metal framework, with one bridging carbonyl ligand between Mn and Co2. The capping CCO moiety is nearly linear (C1–C2–O2 = 177.7 (3)°) and tilts 14° toward Co1, away from the perpendicular to the $MnCo_2$ plane, as determined by CHEMGRAF.

The reaction between $Mn(CO)_5(CX_3)$ and $[PPN][Co(CO)_4]$ possesses several interesting features. One mole of the Mn complex consumes only 1.7 mole of the Co anion, not 2 moles as the stoichiometry of the product indicates. The reaction products other products, $Mn(CO)_5X$ and CoX_2, which may explain the observed stoichiometry as well as the low yield. The product $Mn(CO)_5X$ was identified by IR and mass spectra and has been detected previously in homolytic reactions of $Mn(CO)_5(CX_3)$.[12]

Ketenylidene complexes appear to form under conditions which generate an exposed three-coordinate carbide atom. This proposed carbide appears to be unstable with respect to migration of a CO onto the carbide to form the ketenylidene ligand CCO.[13-15] The source of the capping carbon atom in the reaction of $Mn(CO)_5(CX_3)$ with $Co(CO)_4^-$ is the trihalomethyl ligand on Mn, so all the halides must be removed from carbon in the course of the reaction. By analogy with the reaction of RCX_3 with $Co(CO)_4^-$ which is known to yield $Co_3(CO)_9(\mu_3\text{-}CR)$ complexes,[16] $Co_3(CO)_9(\mu_3\text{-}C\text{-}Mn(CO)_5)$ is a likely intermediate in the formation of 1 (see Scheme I). The formation of this intermediate explains the absence of halides on the capping carbon atoms. Metal-exchange reactions between $Co_3(CO)_9(\mu_3\text{-}CR)$ and metal fragment to form Co_2M complexes are well-known.[17-19] Thus, a metal exchange reaction

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(6) Anal. Calcd for $C_{47}H_{30}O_{10}P_2NMnCo_2$: C, 56.25; H, 3.01; N, 1.40; Mn, 5.84; Co, 11.75. Found: C, 55.90; H, 3.29; N, 1.37; Mn, 5.52; Co, 11.55. IR ($(C_2H_5)_2O$): 2060 (w), 1999 (s), 1987 (sh), 1928 (m) cm^{-1}. 1 was enriched with ^{13}CO by using $PPNCo(^{13}CO)_4$ in its preparation. The capping carbon was not enriched. ^{13}C NMR: δ 215.5 (metal framework CO's), 170.5 (ketenylidene CO).

(7) Crystal data for $[PPN][MnCo_2(CO)_9(CCO)]$: a = 14.859 (4) Å, b = 9.209 (1) Å, c = 16.701 (3) Å, α = 90.08 (2)°, β = 102.79 (2)°, γ = 89.99 (2)°; V = 2228.64 A^3; space group $P\bar{1}$; Z = 2, d_{calc} = 1.495 g/cm^3; μ = 11.296 cm^{-1}; Mo Kα radiation, λ = 0.710 73 Å; 10736 unique reflections, 7960 with $I > 3\sigma(I)$; ω–2θ scan mode; 2.5–55° = 2θ; T = −90 °C; Enraf-Nonius CAD-4 diffractometer. The structure was solved with MULTAN, and subsequent non-hydrogen atoms were located by difference Fourier techniques. The full-matrix least-squares refinement included anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on the phenyl rings were added in calculated positions and were included in the structure factor calculation but were not refined: R_F = 0.047; R_{wF} = 0.056. All calculations were performed on a Digital Equipment Corp. VAX 11/730 computer using the Enraf-Nonius SDP library and the Molecular Structure Corp. TEXLS full-matrix least-squares program.

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between Co and Mn is likely. A two-electron reduction concomitant or subsequent to the metal exchange is necessary to balance the charge. The reducing agent is assumed to be $Co(CO)_4^-$.

The cluster-building reaction to form 1 is highly dependent on the cation associated with $Co(CO)_4^-$. The reaction of $Mn(CO)_5(CBr_3)$ with $NaCo(CO)_4$ yields $Mn(CO)_5Br$ and $Co_4(CO)_{12}$, with no formation of 1. When the cation is PPh_4^+ or Et_4N^+, 1 forms, but in very low yield. When $Mn(CO)_5(CCl_3)$ is used in place of $Mn(CO)_5(CBr_3)$, the reaction proceeds much more slowly, in about 3 h at room temperature. The reaction is also highly solvent dependent. When tetrahydrofuran is used in place of dichloromethane, no reaction takes place.

The ketenylidene complex 1 reacts rapidly with 1 equiv of HSO_3CF_3 at room temperature (eq 3). Proton attack

$$[\mathrm{PPN}][\mathrm{MnCo_2(CO)_9}(\mu_3\text{-}\mathrm{CCO})] + \mathrm{HSO_3CF_3} \rightarrow \mathrm{MnCO_2(CO)_{10}}(\mu_3\text{-}\mathrm{CH}) + \mathrm{PPNSO_3CF_3} \quad (3)$$

occurs at the capping carbon atom, to produce a methylidyne complex, $MnCo_2(CO)_{10}(\mu_3\text{-CH})$ (**2**).[20] This mode of reactivity is typical for negatively charged ketenylidene complexes of the first-row transition metals.[15,21]

In summary, the trihalomethyl transition-metal complexes $Mn(CO)_5(CX_3)$ (X = Cl, Br) have been used successfully to form a mixed-metal cluster containing at a ketenylidene ligand in which the α-carbon atom is derived from the CX_3 moiety. Further cluster building reactions are under investigation.

Acknowledgment. Support for this research was provided by the NSF. A.M.C. thanks Steven Sunshine for crystallographic advice.

Supplementary Material Available: Listings of observed and calculated structure factors, positional and anisotropic thermal parameters, and bond distances and angles (106 pages). Ordering information is given on any current masthead page.

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[20] Anal. Calcd for $C_{11}HO_{10}MnCo_2$: C, 28.35; H, 0.21; Mn, 11.79; Co, 25.30. Found: C, 28.13; H, 0.49; Mn, 11.82; Co, 25.16. IR (hexane): 2061 (s), 2050 (vs), 2002 (w), 1978 (m), 1920 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.37. Mass spectrum: *m/e* 466 (parent peak), successive loss of 10 CO's.

[21] Kolis, J. W.; Holt, E. M.; Hriljac, J. A.; Shriver, D. F. *Organometallics* **1984**, *3*, 496.

Ruthenium-Catalyzed Acrylate Dimerization[†]

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Received May 12, 1986

Summary: Treatment of $(\eta\text{-}C_6H_6)(MA)_2Ru^0$ (MA = $CH_2{=}CHCO_2CH_3$) with 2 equiv of sodium naphthalenide in tetrahydrofuran generates a homogeneous species which selectively catalyzes the dimerization of methyl acrylate (MA) to dimethyl hexenedioate.

The selective tail-to-tail dimerization of acrylates (eq 1) is attractive both as an alternative to the currently practiced cyclohexane oxidation in the synthesis of adipic acid (an important nylon intermediate) and as an intermediate in fine chemicals synthesis.[1]

Table I. Catalyst Activity and Selectivity in Methyl Acrylate Dimerization

cat.	methyl acrylate convn,[a] %	selectivity, % dimer	selectivity, % linear: branched[b]
$RuCl_3{\cdot}3H_2O$[c]	<0.1		
$(C_6H_6)(MA)_2Ru^0$ (1)	12	50	9:1
1 + $2NaC_{10}H_8$[d]	47	77	49:1

[a] At 140 °C for 1 h; [Ru] = 0.010 M; [MA] = 5.4 M in *N*-methylpyrrolidone with decane as internal standard. [b] Linear = dimethyl hexenedioate; branched = head-to-tail dimer, dimethyl α-methylpentenedioate. [c] Methanol ~5% v/v. [d] $(C_6H_6)(MA)_2Ru^0$ treated with 2 equiv of sodium naphthalenide (THF).

$$\underset{\mathrm{MA}}{2\mathrm{CH_2{=}CHCO_2CH_3}} \rightarrow \underset{\mathrm{DHD}}{\mathrm{CH_3O_2CCH{=}CHCH_2CH_2CO_2CH_3}} \quad (1)$$

Previously Alderson, Jenner, and Lindsey[2] reported that $RuCl_3{\cdot}3H_2O$ catalyzes the dimerization of acrylates in the presence of methanol. Our continuing studies of this system[3] have shown that zerovalent ruthenium complexes such as $(\eta\text{-}C_6H_6)(CH_2{=}CHCO_2CH_3)_2Ru^0$ (1) or $(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)Ru^0$ catalyze the same reaction in the absence of additives under milder conditions (140 °C vs. 210 °C) (see Table I).[4]

Kinetic studies using 1 as catalyst precursor reveal that the rate of DHD formation obeys the rate law

$$d[\mathrm{DHD}]/dt = k[\mathrm{Ru}]^{0.5}[\mathrm{MA}]$$

A simple model consistent with this rate law is given by eq 2–4. Equation 2 shows an equilibrium consisting of

$$\mathrm{Ru}_x \rightleftharpoons \mathrm{Ru} + \mathrm{Ru}_{x-1} \quad (2)$$

$$\mathrm{Ru} + \mathrm{MA} \rightarrow \mathrm{Ru'} + \mathrm{DHD} \quad (3)$$

$$\mathrm{Ru'} + \mathrm{MA} \rightarrow \mathrm{Ru} \quad (4)$$

fragmentation of a cluster containing at least two ruthenium nuclei. Equation 3, showing a second-order reaction between one of the ruthenium fragments and MA, is rate limiting. Equation 4 balances the system by adding the second acrylate in a fast step. The half-order dependence on the catalyst results when the equilibrium of eq 2 lies far to the left side.[5] Solvent polarity has a dramatic effect on the catalytic activity with higher activity being favored by very polar, weakly coordinating solvents such as *N*-methylpyrrolidone (NMP). This led us to postulate that the fragmentation is ionic in nature and, since we start with zerovalent ruthenium, suggests one of the fragments may be anionic.

[†] Contribution No. 3733.

[1] For example see: Nugent, W. A.; Hobbs, F. W., Jr. *J. Org. Chem.* **1983**, *48*, 5364.

[2] Alderson, T.; Jenner, E. L.; Lindsey, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 5638. Alderson, T.U.S. Patent 3013066, 1961.

[3] McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080.

[4] McKinney, R. J. U.S. Patent 4485256, 1984.

[5] ^1H NMR studies reveal that coordinated benzene of 1 is irreversibly lost at 90 °C, apparently allowing a dimer or higher cluster to rapidly form.

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