triosmium carbonyl system.[15] $[TaCp'Cl_2H]_2$ reduces acetonitrile especially easily simply because it also easily reduces carbon monoxide, a much more difficult feat.

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Registry No. $[TaCp'Cl_2H]_2$, 74153-80-3; $Ta_2Cp'_2Cl_4(H)(NCHMe)$, 80514-61-0; $Cp'Cl_2\overline{TaCH_2CH_2CH_2}$, 80502-36-9; $TaCp'Cl_2(NEt)$, 80502-37-0.

Supplementary Material Available: Listings of anisotropic thermal parameters and positional parameters (and esd's) and observed and calculated structure factors (×10) for $[Ta(C_5Me_4Et)Cl_2]_2(H)(NCHMe)$ (31 pages). Ordering information is given on any current masthead page.

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Evidence for Tilted Ground-State Structures and Fluxionality in $Co_3(CO)_9CCHR^+$

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Summary: The synthesis and variable-temperature NMR properties of $Co_3(CO)_9CCHCHMe_2^+$ are described. At −65 °C the methyl groups are anisochronous, consistent with a tilted but not with an upright structure. Coalescence of the methyl signals at higher temperatures reflects enantiomerization of the cluster, presumably by disrotatory correlated rotation (gearing) about the $Co_3(CO)_9$–C and C–$CHCHMe_2$ axes. The barrier ($\Delta G^{\ddagger}$) to site exchange is 10.5 ± 0.1 kcal mol^{-1} at −52 °C. The present findings corroborate theoretical predictions by Schilling and Hoffmann.

Among the many interesting properties of the $Co_3(CO)_9C$ cluster is its ability to stabilize adjacent carbenium ions.[2,3] Schilling and Hoffmann[4] have proposed, on the basis of theoretical considerations, that stabilization occurs in $Co_3(CO)_9CCH_2^+$ as a result of the formation of tilted structures **2a** or **3a** rather than the upright structure of type **1a** originally assumed[2,5] (Figure 1). We now report ^{13}C NMR evidence for $Co_3(CO)_9CHCHMe_2^+$ which unambiguously excludes the upright structure and which permits an analysis of the dynamic stereochemistry in this system.

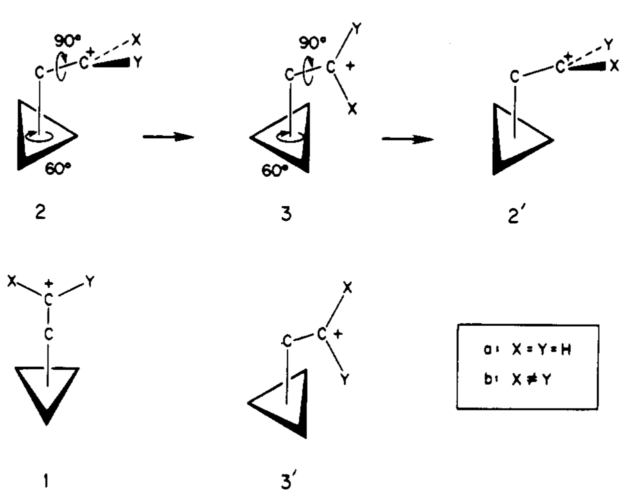

Figure 1. Schematic representation of $Co_3(CO)_9CCXY^+$ conformations. The $Co_3(CO)_9$ triangle is capped by a C–CXY^+ fragment in upright (**1**) or tilted (**2**, **3**) positions. The gearing motion in **2** → **3** → **2′** is shown by the curved arrows.

In **1a** the C_3 axis of $Co_3(CO)_9$ and the C_2 axis of C–CH_2^+ are collinear, leading to a sixfold rotation barrier about the common axis. In the tilted structures, the two axes subtend an angle, and the extended Hückel calculations of Schilling and Hoffmann[4] indicate two stationary points on the potential energy hypersurface. In one (**2a**, C_s) the C^+ bends toward a Co atom and the σ plane bisects the H–C–H angle, whereas in the other (**3a**, C_s) the CH_2 group bends toward the Co–Co bond center and lies in the σ plane. According to Schilling and Hoffmann,[4] **2a** is the ground state, and degenerate isomerization (topomerization) occurs by way of the saddle point **3a**. When X ≠ Y, **2** becomes chiral (**2b**), and the topomerization described above becomes an enantiomerization (**2b** $\rightleftarrows$ **2′b**) by way of achiral transition states **3b** or **3′b**. On the other hand, **1b** is expected to be achiral (the approximately sixfold barrier ensures that any chiral conformation has a negligible lifetime on the NMR timescale). Under conditions of slow enantiomerization, a probe testing for chirality therefore allows a distinction between **1b** and **2b**. The isopropyl group in the derivative with X = H and Y = *i*-Pr is such a probe: in **1b** and **3b** (or **3′b**), the methyls are enantiotopic on the NMR timescale and hence isochronous, whereas in **2b** they are diastereotopic and therefore anisochronous (barring accidental isochrony).

The unsaturated (alkylidyne)tricobalt complex **4**,[6] required as a precursor to $Co_3(CO)_9CCHCHMe_2^+$, was prepared in 14% yield (after extensive purification) by the treatment of 1,1,1-trichloro-3-methyl-2-butene (**5**)[7] with $Co_2(CO)_8$ in the usual method for the preparation of $Co_3(CO)_9CR$ complexes.[8] The required trichloromethyl compound **5** was obtained by careful dehydrobromination of 1,1,1-trichloro-3-bromo-3-methylbutane (**6**).[9]

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(6) ^1H NMR of **4** (CD_2Cl_2): δ 1.87 (s, 3 H), 1.83 (s, 3 H), 7.53 (m, 1 H). Anal. Calcd for $C_{14}H_7Co_3O_9$: C, 33.90; H, 1.42. Found: C, 34.08; H, 1.41.

(7) Nesmeyanov, A. N.; Freidlina, R. Kh.; Zakharkin, L. I.; Belyavskii, A. B. *Zh. Obshch. Khim.* **1956**, *26*, 1070. ^1H NMR of **5** (CCl_4): δ 1.85 (m, 3 H), 2.10 (m, 3 H), 6.25 (m, 1 H).

(8) (a) Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organomet. Chem.* **1973**, *50*, 265. (b) Seyferth, D.; Eschbach, C. D.; Williams, G. H.; Hung, P. L. K. *Ibid.* **1977**, *134*, 67.

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$$H_2C{=}C(CH_3)_2 \xrightarrow[\text{AIBN, 60 °C}]{CCl_3Br} \underset{6}{Cl_3CCH_2C(CH_3)_2Br} \xrightarrow[\text{THF, -40 °C}]{KO\text{-}t\text{-}Bu}$$

$$\underset{5}{Cl_3CCH{=}C(CH_3)_2} \xrightarrow[\text{THF, 35 °C}]{Co_2(CO)_8} \underset{4}{Co_3(CO)_9CCH{=}C(CH_3)_2}$$

When **4** is dissolved in fluorosulfonic acid, it undergoes protonation and forms $Co_3(CO)_9CCHCHMe_2^+$.[10] As the temperature is lowered, the isopropyl methyl ^{13}C resonance, a single peak at δ 24.2 at room temperature, broadens; at −65 °C two peaks of equal intensity are observed at 25.8 and 22.1 ppm. The barrier to site exchange of the methyl groups can be estimated from the coalescence temperature (−52 ± 2 °C) as $\Delta G^* = 10.5 \pm 0.1$ kcal mol^{-1}.

These results are consistent with **2** as the most stable structure, but not with **1** or **3**.[11] The observed coalescence corresponds to a process of enantiomerization for which two diastereomeric transition states, **3b** and **3′b**, need be considered. The observed barrier corresponds to the one lower in energy; this is presumably **3b** since in **3′b** a bulky *i*-Pr group is compressed against the $Co(CO)_3$ groups. By the same token, the magnitude of the barrier in **3b** should be similar to that in **3a**, since the bulky *i*-Pr group is now out of the range of repulsive nonbonded interactions. The rough agreement between the barriers calculated for **3a** (16 kcal mol^{-1} as an upper limit[4]) and found for **3b** is in accord with this supposition.

It is appropriate to view $Co_3(CO)_9CCH_2^+$ as an electronically driven bevel gear system in which gearing occurs by disrotatory correlated rotation about the two axes, via **3a** (Figure 1).[12] We particularly note the stereochemical correspondence of this system to 9-benzyltriptycene,[13] in which a twofold rotor (benzyl) and a threefold rotor (triptycene) undergo an analogous internal rotation. The major difference between the two systems lies in the coupling mechanism, since the forces governing the internal motions in 9-benzyltriptycene are nonbonded interactions.

The transition-metal-stabilized cations $Co_3(CO)_9CCHR^+$ are thus not true three-coordinate carbenium ions but are stabilized by direct interaction between the cationic carbon and the metal framework. A similar conclusion, suggested by similar use of isopropyl diastereotopism as a chirality probe, has already been reached for the other principal class of transition-metal-stabilized carbocations, the ferrocenyl derivatives $FcCHR^+$,[14] and has been confirmed by X-ray structure determinations.[15]

Acknowledgment. We thank the National Science Foundation (Grant CHE 79-20373 to J.R.N. at Colorado State and Grant CHE 80-09670 to K.M. at Princeton) for support of this work and Professor A. I. Meyers for valuable advice on the dehydrobromination of **6**.

Registry No. 4, 80662-57-3; **5**, 80658-25-9; **6**, 23153-21-1; $Co_3(CO)_9CCHCHMe_2^+$, 80662-56-2; $Co_2(CO)_8$, 10210-68-1.

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[9] Kharasch, M. S.; Reinmuth, O.; Urry, W. H. *J. Am. Chem. Soc.* **1947**, *69*, 1105. ^1H NMR of **6** (CCl_4): δ 2.08 (s, 6 H), 3.56 (s, 2 H).

[10] ^1H NMR (FSO_3H): δ 1.54 (d, J = 6 Hz, 6 H), 2.18 (m, 1 H), 6.58 (d, J = 9 Hz, 1 H), referenced to CH_2Cl_2 (δ 5.32) as internal standard. $^{13}C\{^1H\}$ NMR (FSO_3H): δ 24.2 (*Me*$_2$CHCH), 42.0 (Me_2*C*HCH), 131.6 (Me_2CH*C*H), 193 (CO), referenced to CH_2Cl_2 (δ 53.8) as internal standard. At −36 °C another resonance can be seen at δ 272.0 (apical C). Assignments were confirmed by off-resonance decoupling.

[11] There are other possibilities which cannot be ruled out on the basis of the NMR evidence alone (for example, a structure in which the CH_2 group in $Co_3(CO)_9CCH_2^+$ bends toward the center of a Co–Co bond and the σ plane bisects the H-C-H angle), though they are unlikely on theoretical grounds.[4]

[12] The NMR data do not rule out uncorrelated rotation (i.e., rotation of the $CHCHMe_2$ fragment without concomitant rotation of the $Co_3(CO)_9$ moiety), though once again[11] this is unlikely on theoretical grounds.[4]

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Silicon in Synthesis. Ring Expansion and 1,4 Difunctionalization Using Silylcyclopropanes

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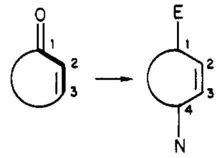
Summary: **Treatment of 7-trimethylsilyl-substituted bicyclo[4.1.0] carbinols with electrophiles leads to ring expansion into an cycloheptenylallylsilane, which can undergo further transformations into substituted cycloheptene derivatives.**

The general formulation shown depicts a complicated overall transformation involving one carbon ring expansion of a cyclic enone, combined with the introduction of an electrophile and nucleophile in a 1,4 relationship to one another.



Here we describe a short and flexible way of carrying out this transformation for the cyclohexenone to cycloheptene system, that utilizes the combined chemistry of silylcyclopropanes,[1] cyclopropylcarbinyl rearrangements,[2] and allylsilane electrophilic substitution.[3] It was envisioned that a (silylcyclopropyl)carbinol, **1**, would readily rearrange under electrophilic conditions via **1a** to give **1b**, where the carbenium ion is now situated β to the tri-

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[1] For the synthesis of silylcyclopropyl ketones using the ylide $Me_3SiCHSMe_2$ and references to silylcyclopropanes see: Cooke, F.; Magnus, P.; Bundy, G. L. *J. Chem. Soc., Chem. Commun.* **1978**, 714.

[2] Cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangements Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1976**, *98*, 7026. Friedrich, E. C.; Jassawalla, J. D. C. *J. Org. Chem.* **1979**, *44*, 4224. For a comprehensive review describing cyclopropane ring opening see: Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577. Hanack, M.; Schneider, H.-J. *Ibid.* **1967**, *6*, 666. Solvolytic rearrangement route to ring-expanded steroids: Steinberg, N. G.; Rasmusson, G. H.; Reamer, R. A. *J. Org. Chem.* **1979**, *44*, 2294. Marshall, J. A.; Ellison, R. H. *Ibid.* **1975**, *40*, 2070. Hudrlik, P. F.; Rudnick, L. R.; Korzeniowski, S. H. *J. Am. Chem. Soc.* **1973**, *95*, 6848. Whalen, D. L.; Cooper, J. D. *J. Org. Chem.* **1978**, *43*, 432. For a general review of cyclopropane chemistry see: Meijere, A.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. Other examples of cyclopropanes in ring expansion reactions: Kohout, L.; Fajkos, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 1613. Bellamy, A. J.; Whitham, G. H. *Tetrahedron* **1968**, *24*, 247. Caine, D.; Gupton, J. T. *J. Org. Chem.* **1974**, *39*, 2654. Seebach, D.; Braun, M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 49. Reese, C. B.; Shaw, A. *J. Am. Chem. Soc.* **1970**, *92*, 2566. Parham, W. E.; Schweizer, E. E. *Org. React.* **1963**, *13*, 55. Amice, P.; Blanco, L.; Conia, J. M. *Synthesis* **1976**, 196.

[3] Pillot, J.-P.; Dunogue's, J.; Calas, R. *Tetrahedron Lett* **1976**, 1871. Fleming, I.; Paterson, I. *Synthesis* **1979**, 445. For a recent review see: Chan, T. H.; Fleming, I. *Ibid.* **1979**, 761.

[4] Friedrich, E. C.; Jassawalla, J. D. C. *J. Org. Chem.* **1979**, *44*, 4224. Describe the cyclopropane walk process for a number of bicyclo[4.1.0] systems.