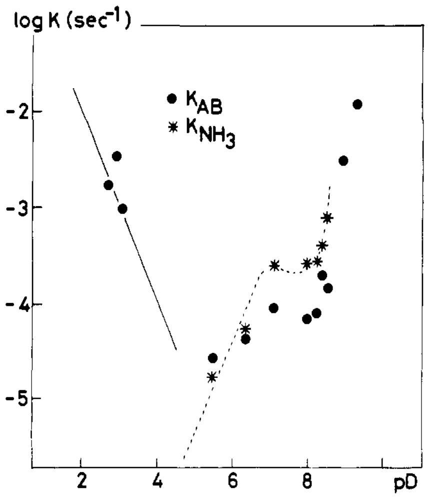

Figure 3. The log (k_{AB}) and log (k_{NH_3}) (deuteration rate of amine group) vs. pD plots for *cis*-K[Co(mal)$_2$(NH$_3$)$_2$].

not H_N that exchanges first with deuterium. Over the whole pD range examined, no change in chemical shift[5] and spin-spin coupling constant[8] was observed.

The origin of the stereoselectivity is not readily apparent.[9] The origin of the reversal of stereoselectivity appears, however, to be explained as follows. It is seen in Figure 2 that the reversal is brought about by an anomalous decrease in k_{HN} and the steady increase in k_{HO} with pD. Next, we note in Figure 3 that, at a pD value of ~7.5, wherein the reversal happens for *cis*-(NH$_3$)$_2$ compound, the deuteration rate of NH$_3$ (k_{NH_3}) exceeds that of CH$_2$ (k_{AB}), but both rates begin to be suppressed. Now, at lower pD values the exchange of amine hydrogens is slower than that of CH$_2$ hydrogens and can not compete with the latter process. If, however, k_{NH_3} increases to a comparable magnitude with k_{AB},[10] amine exchange can interfere with the CH$_2$ change and both amine and CH$_2$ hydrogens scramble for the OD$^-$ catalysis. As a result, both rates will tend to fall together. Even under such circumstances, the deuteration rate of H_O may well be little affected by such competition, because of this proton being situated farthest apart from the amine group, Only the H_N hydrogen, being adjacent to the amine group, pertains to the scrambling for the catalysis, which is consistent with the anomalous decrease of only k_{HN} in Figure 2. Some support to this view seems to be provided by the observation that the reversal did not take place for *N,N'*-dmen, tn, *cis*-py$_2$, and phen compounds. In the first two complexes, exchange rates of amine hydrogens were slower than CH$_2$ exchange and the last two compounds lack exchangeable amine hydrogens.

Acknowledgments. One of the authors (U.S.) acknowledges financial support from The Ministry of Education under Grant No. 446-7054-364214 and The Matsunaga Research Grant.

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(2) (a) H. Yoneda and Y. Morimoto, *Inorg. Chim. Acta*, 1, 413 (1967); (b) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967); (c) M. E. Farago and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 2120 (1972).
(3) All the NMR data were collected at 36 °C and 60 MHz. The pD values refer to apparent pH meter readings.
(4) Abbreviation: mal = malonate ion, en = ethylenediamine, *N,N'*-dmen = *N,N'*-dimethylethylenediamine, tn = trimethylenediamine, py = pyridine, and phen = phenanthroline.
(5) The δ values from internal DSS for H_N and H_O are 3.64 and 3.12, 3.60, and 3.08, 3.67 and 3.14, 3.68 and 3.17, 3.90 and 3.13, and 4.06 and 3.39 for en, tn, *N,N'*-dmen, *cis*-(NH$_3$)$_2$, *cis*-py$_2$, and phen complexes, respectively. Since the variation $\delta(H_N)$ is greater and is affected by nitrogen ligands to a greater extent than $\delta(H_O)$, H_N may be closer to coordinating nitrogen.
(6) Apart from small isotope shifts. In the *cis*-py$_2$ compound, a negative isotope shift (downfield shift) was found for H_N, −0.61 and +1.58 Hz for H_N and H_O, respectively.
(7) In this equation we assumed *no* kinetic isotope effect.
(8) The *J* values for all of the complexes examined in this work are almost the same, 18.4 ± 0.4 Hz.
(9) Since the degree of stereoselectivity, defined as the ratio k_{HN}/k_{HO}, is highest for *N,N'*-dmen and en compounds, followed by tn and *cis*-(NH$_3$)$_2$ compounds, and since *cis*-py$_2$ and phen complexes exhibited little or no stereoselectivity, it appears that stereochemically rigid amine group is essential in realizing the stereoselectivity.
(10) The OD$^-$ ion is known to catalyze the amine hydrogen exchange. See, e.g., U. Sakaguchi, K. Maeda, and H. Yoneda. *Bull. Chem. Soc. Jpn.*, **49**, 397 (1976), and references cited therein.

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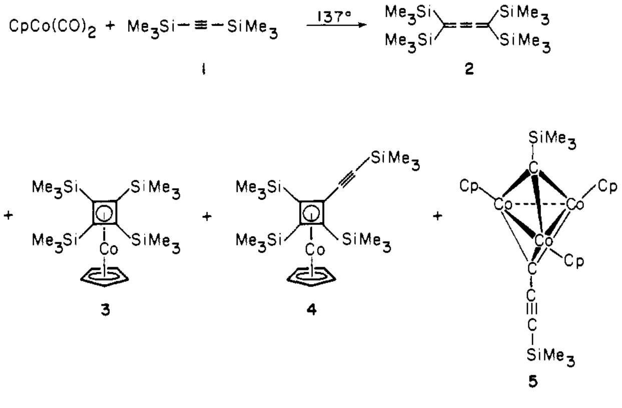
Received November 28, 1978

Apparent Concurrent Acetylene–Vinylidenecarbene Rearrangements, Silyl–Acetylide Metathesis, and Alkyne Cleavage in the Interaction of Bis(trimethylsilyl)acetylene with (η^5-C$_5$H$_5$)Co(CO)$_2$. Crystal and Molecular Structure of a Novel Biscarbyne Complex: [$\mu_3\eta^1$-CSi(CH$_3$)$_3$][$\mu_3\eta^1$-C$_3$Si(CH$_3$)$_3$][(η^5-C$_5$H$_5$)Co]$_3$

Sir:

We have recently utilized neat bis(trimethyl)silylacetylene (**1**) as a hindered co-oligomerization partner in cobalt-catalyzed reactions with diynes to effect chemospecificity and allow introduction of masked functionality (in the form of the trimethylsilyl group) in synthetic methodology leading to complex molecules.[1] Its use was based on the premise that steric factors would prevent reaction of **1** with itself, thereby allowing it to simply coordinate to the metal and eventually enter the cyclization cycle with added diyne. We now report that, on exposure to larger than catalytic amounts of CpCo(CO)$_2$,[2] compound **1** produces a fascinating array of molecular structures (**2–5**)[3] which point to the concurrent operation of several novel reaction pathways traversed by (sterically hindered) acetylenes in the coordination sphere of cobalt. This communication also contains the first report of a crystallographically characterized trinuclear transition metal cluster capped by two triply bridging carbyne ligands.



Tetrakis(trimethylsilyl)butatriene (**2**) was purified by sublimation and preparative gas chromatography[3] and characterized by its spectral data,[4] particularly the ^{13}C NMR spectrum which shows two nonequivalent carbons at characteristically low chemical shifts.[5] The tetrasilylated cyclobutadiene sandwich complex **3** has been obtained previously in low yield (4.7%) as the sole product from the reaction of **6** with **1**.[6] Spectral investigation[4] of the new sandwich **4**[3] revealed the presence of different trimethylsilyl groups in the ratio 2:1:1 by

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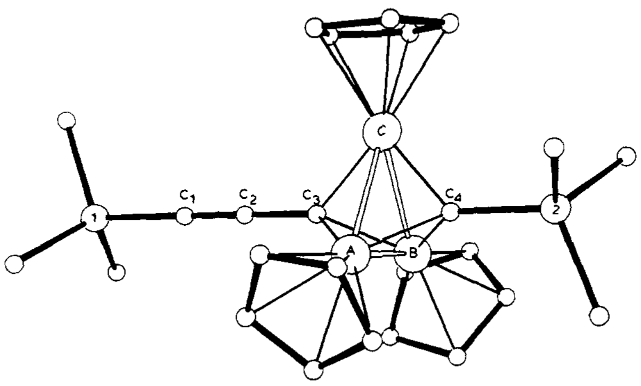
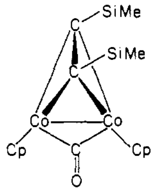


Figure 1. Perspective drawing (adapted from an ORTEP plot) of the $[\mu_3\eta^1\text{-CSi(CH}_3)_3][\mu_3\eta^1\text{-C}_3\text{Si(CH}_3)_3][(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3$ molecule, **5**. Cobalt and silicon atoms are represented by large- and medium-sized open circles labeled with capital letters and numbers, respectively. Carbon atoms are represented by small open circles and all hydrogen atoms are omitted.

^{1}H NMR, and the diagnostic mass spectral fragmentation pattern.[7] Compound **5** was isolated from this reaction in very small quantities.[2-4] The mass spectrum and elemental analysis confirmed the general composition $\text{Me}_3\text{SiC}_4\text{SiMe}_3(\text{CpCo})_3$ which seemed to indicate the formation of a structure of the type **7**. Similar trinuclear metal cluster alkyne complexes had been postulated previously for iron,[8] rhodium,[9] and iridium[9] complexes. However, since the unusual stability and lack of reactivity of our complex (vide infra) appeared to be incompatible with the coordinatively unsaturated nature of **7**, an X-ray crystallographic study of it was undertaken.



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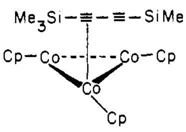

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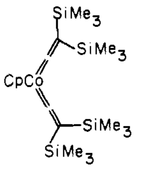

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Large well-shaped air-stable single crystals of **5**, obtained by recrystallization from hexane, are orthorhombic, space group P_{bcn}-D_{2h}[14] (No. 60), with $a = 11.333$ (2) Å, $b = 18.205$ (4) Å, $c = 25.679$ (4) Å, and $Z = 8$ ($d_{\text{calcd}} = 1.421$ g cm^{-3}, $d_{\text{measd}} = 1.412$ g cm^{-3}). Three-dimensional diffraction data were collected on a computer-controlled four-circle Syntex P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (1° wide) ω scans. The structural parameters[11] have been refined to convergence (R (unweighted, based on F) = 0.044 for 2407 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$) in cycles of unit-weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for all nonhydrogen atoms.

The structural analysis shows that crystals of **5** are composed of discrete electron-precise $[\mu_3\eta^1\text{-CSi(CH}_3)_3][\mu_3\eta^1\text{-CC}\equiv\text{CSi(CH}_3)_3][(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3$ cluster molecules (Figure 1) which approximate rather closely C_{3v} molecular symmetry. Each Co atom achieves a filled valence-shell electronic configuration by being bonded to two adjacent Co atoms through 2-electron single bonds, to a cyclopentadienyl (Cp) ligand in a *pentahapto* fashion and to each of the two μ_3-bonded carbyne ligands on opposite sides of the Co_3 triangle. Each of the five-carbon Cp rings are coplanar to within 0.004 Å and their least-squares mean planes intersect the Co_3 triangle in dihedral angles of 92.2-92.4°. Bond lengths and angles for chemically equivalent groupings of atoms, averaged in accord with approximate C_{3v} molecular symmetry, include the following. Bond lengths: Co-Co, 2.383 (2, 9, 14, 3);[12] Co-C (cyclopentadienyl), 2.087 (12, 12, 27, 15);[12] Co-C (carbyne), 1.873 (9, 9, 16, 6); $\text{C}_1\equiv\text{C}_2$, 1.199 (13); C_2-C_3, 1.412 (14); Si-C_1 (or C_4), 1.839 (11, 12, 12, 2) Å. Bond angles: Co-Co-C_9 (Cp center of gravity), 150.0 (-, 9, 16, 6);[12] Si_2-C_4-Co, 132.9 (5, 4, 6, 3);[12] C_2-C_3-Co, 132.5 (7, 1, 1, 3); $\text{C}_1\equiv\text{C}_2$-$\text{C}_3$, 179.0 (10); Si_1-$\text{C}_1\equiv\text{C}_2$, 179.7 (15)°. The $\text{C}_3\cdots\text{C}_4$ contact through the center of the Co_3 triangle is 2.544 (14) Å.

The discovery of products **2**, **4**, and **5** in the reaction of **1** with CpCo(CO)_2 strongly suggests the simultaneous occurrence of several mechanisms. The dimerization path to **2**[13] has as a possible crucial intermediate a bisvinylidene carbene species **8** which could furnish product by reductive elimination. Vinylidene is much more strongly bound to transition metals than π bonded acetylene,[14] and there is precedence for acetylene-vinylidene carbene rearrangements in the coordination sphere of transition metals.[15] The feasibility of biscarbene complexes has also been demonstrated recently in tantalum compounds, although reductive eliminations to give alkenes could not be effected.[16]

Compounds **4** and **5** appear to be products derived from intermediately generated bis(trimethylsilyl)butadiyne (not detectable by FID-GC in starting material **1**). For example, **5** can be made in good yield (65%) by addition of diyne (1 equiv) and CpCo(CO)_2 (3 equiv) to boiling cyclooctane (see, however, ref 7b). An attractive mechanism for diyne formation from **1** involves formal "silyl-acetylide metathesis": $2\text{Me}_3\text{Si}{-}{\equiv}{-}\text{SiMe}_3 \rightleftharpoons \text{Me}_3\text{Si}{-}\text{SiMe}_3 + \text{Me}_3\text{Si}{-}{\equiv}{-}{\equiv}{-}\text{SiMe}_3$. Although palladium-catalyzed disilane metatheses have been observed,[17] and trimethylsilyl- and stannylacetylides appear capable of undergoing oxidative insertion into the heteratom-sp-carbon bond,[18] the postulated transformation is unprecedented.

The remarkable facility with which alkyne cleavage ("dichotomy") occurs to furnish **5** from bis(trimethylsilyl)butadiyne points to the strong possibility that this might be a general process in transition metal chemistry[19] not dependent on the presence of electronically activated alkyne ligands.[10] Biscarbyne complexes of the type **5** might also be intermediates responsible for the repeatedly reported[10a,b,20] occurrence of products formally derived from alkyne cleavage and metathesis.[21] However, we have exposed compound **5** to excess bis(trimethylsilyl)butadiyne in boiling decane for prolonged periods of time (30 days) only to recover it unchanged (85%), in addition to (η^5-Cp)Co(η^4-cyclobutadiene) complexes[7b] and cyclic alkyne trimers.[22] Similar reaction with 3 equiv of diphenylacetylene in boiling decalin gave η^4-tetraphenylcyclobutadiene-CpCo as the major product (18% based on Co) in addition to much intractable material, a trace of unreacted **5**, and trace amounts of many incompletely characterized compounds. No evidence for alkyne metathesis could be obtained.

The reported observations significantly expand the range of products obtainable from the reaction of CpCo(CO)_2 with alkynes and point the way to mechanistic, synthetic, and structural investigations currently being initiated in our laboratories.

Acknowledgments. We thank the National Institutes of Health (GM 22479), the National Science Foundation (CHE 76-01783), the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. W-7405 Eng-48, Chevron Research Co., Pressure Chemical Corp., and Silar Laboratories for generous support.

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(2) In a typical reaction, degassed **1** (8 mL) and $CpCo(CO)_2$ (2.15 g) were added to refluxing nitrogen-flushed **1** (74 mL) over a period of 100.5 h using a syringe pump. After additional refluxing (24 h), excess **1** was removed by vacuum transfer and the products were chromatographed on Woelm neutral alumina (grade II) eluting in consecutive fractions (pentane) **2** (540 mg), **3** (1.44 g), **4** (80 mg), and (pentane–ether, 19:1) **5** (7 mg).

(3) Satisfactory analytical and spectral data were obtained for all new compounds.

(4) Compound **2**: pale yellow crystals; mp 103–104 °C; *m/e* 340.1881 (calcd 340.1894, M^+, 70%), 237 ($M - Me_3Si$, 74%), 179 ($M - Me_3Si, -Me_4Si$, 75%), 73 (Me_3Si, 100%); τ (CCl_4) 9.83 (s); ^{13}C NMR (parts per million from Me_4Si, in C_6D_6) δ 0.54, 157.17, 207.03; $\nu_{C=C}$ 1536, ν_{Me_3Si} 1245 cm^{-1}; UV λ_{max} (95% EtOH) 209 (log ϵ 4.60), 282 (4.30), 298 (4.58). **4**: orange crystals; mp 83.5–86.5 °C; *m/e* 488.1609 (calcd 488.1617, M^+, 100%), 318 ($M - Me_3SiC_2SiMe_3$, 6%), 294 ($M - Me_3SiC_4SiMe_3$, 61%); τ (CCl_4) 5.22 (s, 5 H), 9.77 (s, 18 H), 9.86 (s, 9 H), 9.92 (s, 9 H); IR $\nu_{C\equiv C}$ 2125, ν_{Me_3Si} 1250 cm^{-1}. **5**: dark purple crystals: mp 188–189.3 °C; *m/e* 566 (M^+, 20%), 370 (3%), 247 (7%), 189 (Cp_2Co, 100%); τ 5.77 (s, 15 H), 9.27 (s, 9 H), 9.51 (s, 9 H); IR $\nu_{C\equiv C}$ 2070, ν_{Me_3Si} 1240 cm^{-1}.

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(11) The three crystallographically independent cobalt atoms were located through direct methods (MULTAN) and the remaining nonhydrogen atoms of the totally general-position asymmetric unit were located by standard difference Fourier techniques. Further refinement is underway using the more complete ($2\theta_{Mo K\bar{\alpha}} < 54.9°$) data set and a model which incorporates anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all locatable hydrogen atoms.

(12) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

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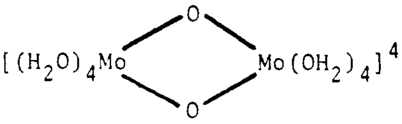
Received January 15, 1979

The Nature of Molybdenum(IV) in Aqueous 4 M HCl Solution. Structure Analysis by EXAFS

Sir:

The structure of Mo(IV) in acidic aqueous media has occasioned much speculation[1-5] since its first synthesis in relatively pure form in 1966.[1] The solution structure of the red ion was originally proposed[1] as $MoO(OH)^+$, but Ardon and Pernick,[4] on the basis of ion-exchange column elution behavior (4 M HPTS) and redox titrations, postulated a dinuclear structure (I). Their conclusion was challenged by Ramasami et al.,[5] whose kinetics data were interpreted in terms of a mononuclear MoO^{2+} or $Mo(OH)_2{}^{2+}$ structure. However, Ardon and co-workers[6] performed cryoscopic experiments that rule strongly in favor of a dinuclear formulation such as I; what is more, the results of recent electrochemical studies[7] are entirely consistent with some type of dimeric structure for $Mo(IV)_{aq}$.



I

X-ray absorption spectroscopy has recently been developed as a probe of molecular structure capable of identifying the type, number, and distances of atoms in the environment of a particular X-ray absorber.[8,9] Analysis of the extended X-ray absorption fine structure (EXAFS) of a variety of Mo compounds has demonstrated an accuracy of ±0.02 Å in the determination of Mo-X distances, along with a capacity for identifying the type and number of X atoms.[10] In this communication we present X-ray absorption data for Mo(IV) in 4 M HCl that (1) conclusively rule out mononuclear formulations and strongly suggest a dinuclear structure; (2) indicate the absence of multiply bound oxo groups; and (3) provide the first quantitative structural information about Mo-Mo and Mo-O bond lengths in this Mo(IV) complex.

The molybdenum K-absorption edge of Mo(IV) in 4 M aqueous HCl is shown in Figure 1a.[11] The principal inflection point occurs at 20014.9 ± 0.5 eV, which is within experimental error of the 20015.4 ± 0.5 eV value previously found for

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