Synthesis, X-ray Structures, and Reactivity of the First Bls(amino)metallastibanes and Bis(amino)metallabismuthanes

Anne-Marie Caminade
Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, F-31077 Toulouse Cedex, France

Michael Veith* and Volker Huch
Institut für Anorganische Chemie der Universität, Im Stadtwald, D-6800 Saarbrücken, West Germany

Wolfgang Malisch*
Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, West Germany

Received September 12, 1989

Introduction

Organometallic complexes of the main-group elements are attracting an increasing amount of interest. For example, a significant number of metallaphosphanes, L₃M(PR₃)₃ (M = transition metal) have been synthesized and structurally characterized.1 However, few investigations deal with the analogous compounds of the heaviest group-15 elements, i.e., metallastibanes2 and metallabismuthanes,3,4 Such derivatives have been known since 1964,3,5 but organic substituents of antimony and bismuth lack diversification as in most cases, alkyl or phenyl groups, sometimes halides, but no amino groups have been used. Moreover, only one structure, PPh₃(CO)₉CoBiPPh₃, has been determined by X-ray diffraction so far.3e

This paper reports the synthesis of the first amino-substituted metallastibanes and bismuthanes, their single-crystal X-ray diffraction characterization, and their behavior toward Fe₂(CO)₉.

Results and Discussion

Synthesis of Metallastibanes and Metallabismuthanes. The reaction of Me₃Sb(N-t-Bu)₂ECI (E = Sb, Bi) with NaM(CO)₅Cp (M = Fe, Mo, W; Cp = η⁵-C₅H₅) affords metallastibanes and bismuthanes, Cp(CO)₅M(Nt-Bu)₂SbMe₅ (4a–c, 5a–c). The structures of 4c (E = Sb, M = W) and 5e (E = Bi, M = W) have been determined by X-ray crystallography. Both compounds are isotopic and isostuctural and crystallize in the triclinic space group with a = 7.830 (9) Å, b = 5.51 (1) Å, c = 16.22 (2) Å, α = 94.1 (1)°, β = 90.4 (1)°, γ = 104.9 (1)°. Z = 2 for 4c and a = 7.014 (9) Å, b = 10.57 (1) Å, c = 16.25 (2) Å, α = 94.1 (1)°, β = 90.1 (1)°, γ = 104.6 (1)°, Z = 2 for 5e. The E–W σ-bond lengths are 3.010 (1) Å for E = Sb and 3.082 (1) Å for E = Bi. The reaction of the binary derivatives with Fe₂(CO)₉ yields [Fe₂(CO)₉]Cp(CO)₅Sb(N-t-Bu)₂SbMe₅ (6a–c) as a result of the complexation of the antimony lone pair. The crystal structures of 6a (M = Fe) and 6b (M = Mo) have been determined. 6b crystallizes in the monoclinic space group with a = 10.399 (9) Å, b = 16.76 (2) Å, c = 15.74 (1) Å, β = 94.16 (6)°, and Z = 4. Both Sb–Fe bond lengths are almost identical: 2.547 (1) Å for the covalent bond and 2.530 (1) Å for the dative bond. 6b crystallizes in the monoclinic space group with a = 12.305 (7) Å, b = 13.812 (7) Å, c = 16.75 (1) Å, β = 93.93 (5)°, and Z = 4. The Sb–Mo covalent bond length is 2.871 (1) Å and the Sb–Fe dative bond 2.539 (1) Å.

Scheme I

| 1 | E = Sb | 3a : M = Fe, n = 2 |
| 2 | E = Bi | 3b : M = Mo, n = 3 |
| 4a–c : E = Sb |
| 5a–c : E = Bi |

The reaction of Me₃Sb(N-t-Bu)₂ECI (E = Sb) and 2 (E = Bi),4 in hexane or benzene solution with NaM(CO)₅Cp to yield 3a–c (M = Fe, Mo, W), at room temperature, yields, by a nucleophilic metation process, the corresponding cyclic bis(amino)metallastibanes, 4a–c, and -bismuthanes, 5a–c (Scheme I).

'H NMR spectroscopy shows that crude 4a–c and 5a–c are quantitatively obtained. Compounds 4a–c and 5b–c are isolated in 46–71% yield as extremely air- and moisture-sensitive powders or crystals. The sensitivity is related at least in part to the high lability of the E–N bonds, which are easily cleaved to give bis(tert-buty1amino)dimethylsilane. The most labile compound is 4b, which has not been isolated but only characterized in solution. Its 'H NMR spectrum shows a strong signal in the range expected for such a compound: 0.19 and 0.39 ppm for the...
Metallastibanes and Metallabismuthanes

Table I. 'H NMR and IR Data for Compounds 4a-c, 5a-c, and 6a-c

<table>
<thead>
<tr>
<th>compound</th>
<th>Me tBu Cp</th>
<th>IR, v(CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂Si(N-t-Bu)₂SbFe(CO)₃Cp</td>
<td>0.35 1.19 4.28</td>
<td>1982 (s), 1933 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂SbMo(CO)₃Cp</td>
<td>0.47 1.20 4.73</td>
<td>1985 (e), 1917 (m), 1588 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂SbW(CO)₃Cp</td>
<td>0.41 1.19 4.77</td>
<td>1987 (s), 1916 (m), 1583 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiFe(CO)₃Cp</td>
<td>0.45</td>
<td>1585 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.19 1.13 4.45</td>
<td>1976 (s), 1929 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiW(CO)₃Cp</td>
<td>0.28 1.14 4.86</td>
<td>1982 (a), 1910 (w), 1578 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.35</td>
<td>1878 (s)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiW(CO)₃Cp</td>
<td>0.24 1.14 4.95</td>
<td>1983 (s), 1909 (w), 1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.35</td>
<td>1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiW(CO)₃Cp</td>
<td>0.21 1.14 4.95</td>
<td>1983 (s), 1909 (w), 1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.35</td>
<td>1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiW(CO)₃Cp</td>
<td>0.24 1.14 4.95</td>
<td>1983 (s), 1909 (w), 1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.35</td>
<td>1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiW(CO)₃Cp</td>
<td>0.21 1.14 4.95</td>
<td>1983 (s), 1909 (w), 1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.35</td>
<td>1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiW(CO)₃Cp</td>
<td>0.24 1.14 4.95</td>
<td>1983 (s), 1909 (w), 1878 (m)</td>
</tr>
<tr>
<td>Me₂Si(N-t-Bu)₂BiMo(CO)₃Cp</td>
<td>0.35</td>
<td>1878 (m)</td>
</tr>
</tbody>
</table>

'Spectra were recorded on a solution of the compound in C₄D₆. Hexane solution for 4a-c and 5a-c, benzene for 6a-c.

Figure 1. ORTEP drawing of 4c. Important bond distances (Å) and angles (deg): SiW = 3.081 (1); N(1)Si = 2.050 (7); N(1)Bi = 2.103 (7); N(1)Sb = 2.066 (7); N(1)Si = 1.734 (8); N(2)Si = 1.735 (8); N(1)SbW = 105.7 (2); N(1)SbW = 105.0 (2); N(1)SbN(2) = 74.3 (3); N(1)SIN(2) = 96.9 (3); N(1)Sb = 96.9 (3); N(2)Sb = 96.4 (3).

Two magnetically unequivalent methyl groups, 1.13 ppm for the two equivalent tert-butyl groups, and 4.45 ppm for the π-bonded cyclopentadienyl ring. Furthermore, two intense carbonyl stretching vibrations are present in the IR spectrum of 5a as in the spectrum of the analogous isolated antimony derivative, 4a. Similarly, the IR spectra of 4b,c and 5b,c exhibit three carbonyl stretching vibrations of four-membered 2.066 (7); N(1)Si = 1.734 (8); N(2)Si = 1.735 (8); N(1)SbW = 105.7 (2); N(1)SbW = 105.0 (2); N(1)SbN(2) = 74.3 (3); N(1)SIN(2) = 96.9 (3); N(1)Sb = 96.9 (3); N(2)Sb = 96.4 (3).

To ascertain further the structure of the compounds of types 4 and 5, X-ray structure determinations have been undertaken for 4c and 5c.

X-ray Structural Analysis of 4c and 5c. The results of these determinations appear in Figures 1 for 4c and 2 for 5c, together with the atom-numbering protocol and selected bond lengths and angles. Pertinent crystallographic data are collected in Table II (compounds 4c and 5c are isotypic and isometric).

Both crystal structures consist of distinct, well-separated monomers, which are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation. The four-membered rings N(l)SiN(2) and N(l)E(2) are in perfect agreement with our formulation.
and angles (deg): MoSb = 2.871 (1); FeSb = 2.539 (1); N(1)Sb = 2.054 (7); N(2)Sb = 2.050 (6); N(1)SbFe = 122.8 (1); N(1)SbMo = 108.9 (2); N(2)SbMo = 115.5 (2); N(1)SbFe = 115.0 (2); N(2)SbFe = 114.1 (2); N(1)SbN(2) = 74.5 (3); N(1)SiN(2) = 91.7 (3); SiN(1)Sb = 96.6 (3); SiN(2)Sb = 97.1 (3).

with respect to 1 (274.5°) or 2 (267.4°).

To the best of our knowledge, 4c represents the first structurally characterized example of stibido ligands (and 5e the second for bismuthido ligands) terminaly coordinated to transition-metal centers, and therefore direct comparisons of E-W distances are not possible. The observed E-W distances (3.010 Å for E = Sb and 3.082 Å for E = Bi), although much longer than those described in the literature for dative σ-bonds (e.g., 2.757 and 2.766 Å for \([W(CO)_5]_2(-W(CO)_5)\) [SBH]_2) and 2.851 Å for \([W(CO)_5]_2\) [SBH]_2, and of tungsten (1.611 Å), are close to the sum of covalent radii of antimony or bismuth (1.40 and 1.46 Å, respectively) and of tungsten (1.611 Å) obtained from \(\text{CP}(\text{CO})_3\) \(W(\text{CO})_3\) \(\text{CP}_3\). In comparison to the chlorine compounds 1 and 2, the Si–N distances in 4c and 5c are of the same magnitude (1.73–1.75 Å).

**Complexation of Metallastibanes.** When a benzene solution of metallastibanes 4a–c is added to a benzene suspension of FeSb, the corresponding complexes 6a–c are isolated in 59–62% yield as relatively air-stable compounds (Scheme II).

The reaction of metallabismanthanes 5a–c under the same experimental conditions did not afford the corresponding metallabismanthane complexes. This illustrates the well-known decrease in the availability for bonding of the lone pair with the group-15 elements, on going from phosphorus to bismuth, and may be related to an increase in the s character of the lone pair.

Compounds 6a–c have been fully characterized. A comparison of 1H NMR values (Table I) of free, 4, and complexed, 6b, derivatives shows, as expected, a downfield shift of the methyl and tert-butyl resonances as a result of complexation. A downfield shift is also observed for the cyclopentadienyl signal of 6a, whereas the corresponding value for 6b,c remains essentially unchanged.

**X-ray Structural Analysis of 6a and 6b.** The structures of 6b and 6a are illustrated in Figures 3 and 4, respectively, together with atom-numbering schemes and

---

**Table III. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement for 6a and 6b**

<table>
<thead>
<tr>
<th>6a</th>
<th>6b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>formula</strong></td>
<td>(\text{C}<em>9\text{H}</em>{12}\text{F}_2\text{N}_2\text{O}<em>2\text{Sb}</em>{10})</td>
</tr>
<tr>
<td>(\text{C}<em>9\text{H}</em>{12}\text{FeMoN}_2\text{O}<em>2\text{Sb}</em>{10})</td>
<td></td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>(P2_1/n)</td>
</tr>
<tr>
<td>(Cc)</td>
<td></td>
</tr>
<tr>
<td><strong>(a), Å</strong></td>
<td>10.399 (9)</td>
</tr>
<tr>
<td>12.305 (7)</td>
<td></td>
</tr>
<tr>
<td><strong>(b), Å</strong></td>
<td>16.76 (2)</td>
</tr>
<tr>
<td>13.812 (7)</td>
<td></td>
</tr>
<tr>
<td><strong>(c), Å</strong></td>
<td>15.74 (1)</td>
</tr>
<tr>
<td>16.75 (1)</td>
<td></td>
</tr>
<tr>
<td><strong>(\beta), deg</strong></td>
<td>94.16 (6)</td>
</tr>
<tr>
<td>99.03 (5)</td>
<td></td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td><strong>(V), Å³</strong></td>
<td>2736</td>
</tr>
<tr>
<td>2812</td>
<td></td>
</tr>
<tr>
<td><strong>(d_{\text{calc}}), g/cm²</strong></td>
<td>1.169</td>
</tr>
<tr>
<td>1.736</td>
<td></td>
</tr>
<tr>
<td><strong>crystal dimens, mm²</strong></td>
<td>0.10 × 0.12 × 0.20</td>
</tr>
<tr>
<td>0.12 × 0.15 × 0.25</td>
<td></td>
</tr>
<tr>
<td><strong>radiation</strong></td>
<td>(M_{\text{Cu}}) (0.71069 Å)</td>
</tr>
<tr>
<td>(M_{\text{Cu}}) (0.71069 Å)</td>
<td></td>
</tr>
<tr>
<td><strong>(\mu), cm⁻¹</strong></td>
<td>20.84</td>
</tr>
<tr>
<td>19.52</td>
<td></td>
</tr>
<tr>
<td><strong>no. of unique reflexions measured</strong></td>
<td>3374</td>
</tr>
<tr>
<td>2188</td>
<td></td>
</tr>
<tr>
<td><strong>no. of observed reflexions for refinement</strong></td>
<td>2923 ((F_o &gt; 2\sigma(F_o)))</td>
</tr>
<tr>
<td>2020 ((F_o &gt; 2\sigma(F_o)))</td>
<td></td>
</tr>
<tr>
<td><strong>variables used in refinement</strong></td>
<td>323</td>
</tr>
<tr>
<td>269</td>
<td></td>
</tr>
<tr>
<td><strong>(R)</strong></td>
<td>0.033</td>
</tr>
<tr>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td><strong>(R_w)</strong></td>
<td>0.033</td>
</tr>
<tr>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td><strong>(w = k/\sigma(F) + [g(F)]^2)</strong></td>
<td>(h), unit weight; (g), 1.0; (g), 0.00135</td>
</tr>
<tr>
<td>unit weight</td>
<td></td>
</tr>
<tr>
<td>atoms refined anisotropically</td>
<td></td>
</tr>
<tr>
<td>(\text{Sb, Fe, Si, O, N, C1–C21})</td>
<td></td>
</tr>
<tr>
<td>(\text{Sb, Mo, Fe, Si, O, N, C1–C7, C13, C17})</td>
<td></td>
</tr>
</tbody>
</table>

---


selected bond lengths and angles. Pertinent crystallo-
graphic data are summarized in Table III. Figures 3 and 4 support our assumptions concerning the
complexation of the antimony lone pair by Fe(CO)_4. The
environment around the iron (tetracarbonyl) atom is a
distorted trigonal bipyramid in both structures. The
largest deviation from ideality is found for the SbFeC+
 distorted trigonal bipyramid in both structures. The
complexation of the antimony lone pair by Fe(CO)_4 The
Metallastibanes and Metallabismuthanes Organometallics,
graphic data are summarized in Table 111.

angles: 174.5° for 6a and 175.9° for 6b. Among the six
angles around antimony, only two are far from tetrahedral
values: the FeSbS angles (121.1° for 6a (M = Fe), 122.8°
for 6b (M = Mo)) which are larger than the value found
in the related compound 7 (FeSbFe = 117°) and the

N(1)SbN(2) angles which are identical for the free and
complexed derivatives (74.3° for 4c, 74.7° for 6a, 74.5°
for 6b). On the other hand, complexation affects the average
NSbM angles: 105.3° for uncomplexed 6a, 110.3°
for 6a and 6b, respectively. Another interesting feature of the structure of
6a,b is the covalent bond length Sb-M. If the length is calculated
as for 4c (i.e., the sum of the molybdenum covalent radius
(1.617 Å) obtained from Cp,Mo(CO)_5 and of the antimony
covalent radius (1.40 Å)), the result is 3.017 Å, whereas the actual bond length is 2.871 Å for 6b. Thus,
complexation of the antimony lone pair induces a dramatic
shortening of the Sb-M covalent bond length. This is true
also for 6a since both Sb-Fe bond lengths (2.547 Å for the
covalent bond and 2.530 Å for the dative bond) are almost
equal. We have interpreted the shortening of the covalent
Sb-M bond in terms of an increased amount of M-Sb
back-bonding (the similarity of the Sb-N bond lengths in 4c and 6a,b argues against any noticeable de-
crease in the σ-bonding covalent radius of antimony). This
is also consistent with the downfield shift of the cyclo-
pentadienyl resonance observed in the ^H NMR spectrum of
6a in comparison to 4a.

Experimental Section
All operations were carried out under an atmosphere of dried
nitrogen. Solvents were refluxed over lithium aluminum hydride
for 3 days before distillation and kept over sodium wires.

General Procedure for the Synthesis of [Me,Si(N-t-Bu),SbCl,
Me,Si(N-t-Bu)] and of [Me,Si(N-t-Bu),BiCl], 1, and 2, were prepared as
described in the literature, as was 3a. ^H NMR spectra
were recorded on a Bruker WP-80 instrument. ^H chemical shifts
are reported in ppm relative to MeSi. Infrared spectra
were recorded on a Perkin-Elmer 883 using one NaCl cell, the
solvent spectrum being subtracted from the complex solution
spectrum. Melting points were measured in sealed capillaries.

Molecular weight measurements were carried out in benzene.

General Procedure for the Synthesis of [Me,Si(N-t-
Bu),]2EM(CO),(µ-3,5-C_5H_3)E, 4a-c and 5a-c. Typically a hexane
solution of [Me,Si(N-t-Bu)]Cl (7 $ 10^{-3} mol in 30 mL) was added
dropwise at room temperature to a suspension of Na,CO_3 (2 $ 10^{-3} mol, 70-100% excess) in hexane (10 mL). The
resulting mixture was magnetically stirred. NaCl and excess Na,CO_3 were then removed by filtration. An
extremely air- and moisture-sensitive red solution of Cp(CO),ME-
(N-t-Bu),SiMe_2, 4a-c or 5a-c, was obtained. According to ^H NMR
spectra, yields were nearly quantitative.

6a: Synthesis of 1,3-Di-t-butyl-2,2-dimethyl-4-[(di-
carbonyl-µ-3-cyclopentadienyl)ferroio]-1,3,2,4-diazasilastibetidine,
Cp(CO),FeSb(N-t-Bu),SiMe_2, 4a. The solution of 4a obtained from 0.291 g (0.815 mmol) of Me,Si(N-t-Bu),SiCl_2, 1,
and 0.277 g (1.38 mmol) of Na,Fe(CO),Cp, 3a, was concentrated
under vacuum to 2 mL and cooled to 1 h at 78 °C. 4a
precipitated as an orange solid (0.240 g, 0.651 mmol, 58% yield),
mp 103-105 °C. Calcd mol wt 499 g/mol, found (cycroscopic)
501 g/mol. Anal. Calcd for Cp,HgFe,N,Os,SbSi: C, 40.90; H, 5.87;
N, 5.61. Found: C, 42.49; H, 6.26; N, 4.88.

Synthesis of 1,3-Di-t-butyl-2,2-dimethyl-4-[(tri-
carbonyl-µ-3-cyclopentadienyl)gemyldobenio]-1,3,2,4-diazasi-
lastibetidine, Cp(CO),MoSb(N-t-Bu),SiMe_2, 4b. The solution
of 4b obtained from 0.397 g (1.11 mmol) of Me,Si(N-t-Bu),SiCl,
1, and 0.369 g (2.20 mmol) of Na,Mo(CO),Cp, 5b, was concentrated
under vacuum to ~2 mL and left for 1 day at room temperature.
4b crystallized as small brown needles (0.289 g, 0.511 mmol, 46% yield),
mp 78–80 °C. Calcd mol wt 567 g/mol, found (cycroscopic) 569 g/mol. Anal. Calcd for Cp,HgMo,N,Os,SbSi: C, 38.11; H, 5.16;
N, 4.94. Found: C, 38.13; H, 5.33; N, 4.95.

Synthesis of 1,3-Di-t-butyl-2,2-dimethyl-4-[(tri-
carbonyl-µ-3-cyclopentadienyl)tungstenio]-1,3,2,4-diazasi-
lastibetidine, Cp(CO),Wb(N-t-Bu),SiMe_2, 4c. A 0.650 g (1.46
mmol) sample of Me,Si(N-t-Bu),SiCl, 1, and 0.364 g (2.71 mmol)
of Na,W(CO),Cp, 5c, were reacted to give a solution of 4c, which
was concentrated to ~15 mL and left for 4 h at room temperature.
4c was obtained as orange crystals (0.681 g, 1.04 mmol, 71% yield),
mp 139–141 °C. Anal. Calcd for Cp,Hg,Wb,N,Os,SbSi: C, 32.99;
H, 4.47; N, 4.28. Found: C, 32.92; H, 4.36; N, 4.25. One of these
crystals was suitable for an X-ray structure determination.

Synthesis of 1,3-Di-t-butyl-2,2-dimethyl-4-[(di-
carbonyl-µ-3-cyclopentadienyl)ferroio]-1,3,2,4-diazasilastibetidine,
Cp(CO),FeSb(N-t-Bu),SiMe_2, 6a. The solution
was carried out with 0.237 g (0.633 mmol) of Me,Si(NtBu),BiCl,
2, and 0.203 g (1.01 mmol) of Na,Fe(CO),Cp, 3a, but all attempts
failed. This compound was characterized only by ^H NMR and IR spectra (Table I).

Synthesis of 1,3-Di-t-butyl-2,2-dimethyl-4-[(tri-
carbonyl-µ-3-cyclopentadienylmolybdenio]-1,3,2,4-diazasilastibetidine, Cp(CO),MoSb(N-t-Bu),SiMe_2, 6b. The
solution of 5b obtained from 0.38 g (0.855 mmol) of Me,Si-
(NtBu),BiCl, 2, and 0.418 g (1.06 mmol) of Na,Fe(CO),Cp, 3b,
was slowly concentrated under vacuum. Small brown needles of
5b were deposited on the walls of the flask (0.303 g, 0.47 mmol,
55% yield), mp 130–132 °C. Calcd mol wt 645.5 g/mol, found (cycroscopic) 682 g/mol (probably because of decomposition). Anal. Calcd for Cp,Hg,Bi,N,Os,SbSi: C, 33.08; H, 4.48; N, 4.28. Found:
C, 33.14; H, 4.60; N, 4.12.

Synthesis of 1,3-Di-t-butyl-2,2-dimethyl-4-[(tri-
carbonyl-µ-3-cyclopentadienyltungstenio]-1,3,2,4-diazasilastibetidine, Cp(CO),Wb(N-t-Bu),SiMe_2, 6c. The solution
which
was obtained from 0.397 g (1.11 mmol) of Me,Si(N-t-Bu),SiCl,
1, and 0.277 g (1.38 mmol) of Na,Fe(CO),Cp, 3a, was concentrated
under vacuum to 0.511 mmol, 46% yield), mp 512–515 °C. Calcd mol
wt 501 g/mol, found (cryoscopic) 501 g/mol. Anal. Calcd for
Cp,Hg,Feb,N,Os,SbSi: C, 51.22; H, 2.78; N, 2.95. Found:
C, 51.25; H, 2.81; N, 2.82.
NαFe(CO)₄Cp 3α, and 0.171 g (0.471 mmol) of Fe₂(CO)₉ was dissolved in a mixture of toluene at room temperature; then the solution was cooled at -20 °C, affording red crystals of 6α (0.198 g, 0.297 mmol, 62% yield based upon 1), mp 298-240 °C. Anal. Calcd for C₇₅H₆₃Fe₆Na₃O₁₂Si₂Sb₂: C, 37.81; H, 4.39; N, 3.40. Found C, 37.62; H, 4.35; N, 3.43.

Some crystals (~10⁻⁵ mol) were dissolved in refluxing hexane (25 mL); the solution was filtered, cooled to 0 °C, and left overnight at this temperature, affording red single crystals.

**Synthesis of Tetracarbonyl(1,3-di-t-Butyl-2,2-dimethyl-4-(tricarbonyl-η⁵-cyclopentadienyl)molybdenum)-1,3,2,4-diazasilaazastibidinediron, [Fe(CO)₃Cp(CO)₃MoSb(N-t-Bu)₂SiMe₃]₆b.** Hexane (5 mL) was added to the powder of 6b obtained from 0.208 g (0.582 mmol) of Na₂Mo(CO)₆, 1.0.292 g (1.09 mmol) of Na₂Mo(CO)₆Cp, 3b, and 0.209 g (0.575 mmol) of Fe₂(CO)₉. The resulting brown suspension was vigorously magnetically stirred and then allowed to settle. Solvent was removed by a pipet, and hot toluene (3 mL) was added to the unsoluble material. The resulting mixture was filtered, giving a red solution, which was cooled overnight at -20 °C. 6b was obtained as red crystals (0.269 g, 0.366 mmol, 63% yield based upon 1), mp 238-240 °C. Anal. Calcd for C₂₂H₃₁N₂O₇SbSi: C, 32.10; H, 3.56; N, 3.41. Found C, 32.62; H, 3.65; N, 3.42.

**Ligand-Field and Charge-Transfer Photochemistry of M(CO)₄(1,10-phenanthroline) (M = Cr, Mo, W). Mechanistic Information from High-Pressure Effects**

S. Wieland, K. Bal Reddy, and R. van Eldik*

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, FRG

Received October 12, 1989

The pressure dependence of the quantum yield for photosubstitution of CO in M(CO)₄(1,10-phenanthroline) (M = Cr, Mo, W) was studied at different excitation wavelengths in order to resolve the nature of the substitution mechanism operating from the ligand-field and charge-transfer excited states. Irradiation at 366 nm results in positive volumes of activation (between +6 and +10 cm³ mol⁻¹) for ligand-field photosubstitution, in agreement with a dissociative substitution mode. Irradiation at 546 nm results in significantly negative volumes of activation (between -12 and -14 cm³ mol⁻¹) for charge-transfer photosubstitution in the case of M = Mo and W, which is interpreted as strong evidence for an associative substitution reaction originating from the MLCT excited state. The corresponding value is small positive for the Cr complex and ascribed to a dissociative process operating from the charge-transfer excited state.

**Introduction**

The application of high-pressure kinetic techniques in mechanistic studies on the reactions of inorganic and organometallic complexes in solution has received much attention from various groups in recent years. Especially the application of this method in the elucidation of the mechanisms of thermal reactions has been rather successful. We and others' have in recent years investi-

---

(1) Work performed at the Institute for Physical and Theoretical Chemistry, University of Frankfurt, FRG.
(2) On leave from the Department of Chemistry Osmania University, Hyderabad-500007, India.