Thiocarbonyl Complexes of Rhenium. Part I.
Synthesis, Characterization and X-Ray Structures of
\([\text{Re(CS)(Me}_2\text{PhP)}_3(\text{Et}_2\text{dtc})]\) and \([\text{Re(CS)(Et}_2\text{dtc)}_3]\)

Ulrich Abram*
University of Tübingen, Institute of Inorganic Chemistry, Auf der Morgenstelle 18,
D-W-7400 Tübingen

Bernd Lorenz
Wissenschaftlerintegrationsprogramm (WIP), Permoserstraße 15, D-O-7050 Leipzig

Z. Naturforsch. 48b, 771–777 (1993); received January 26, 1993

Rhenium Compounds, Thiocarbonyl Complexes, Crystal Structure, Mass Spectra, X-Ray

Novel rhenium complexes with terminal thiocarbonyl groups have been synthesized from
\(\text{ReCl}_3(\text{Me}_2\text{P}h\text{P})_3\) and sodium diethyldithiocarbamate. \(\text{mer-}[(\text{diethyldithiocarbamato})\text{thiocarbonyl}]\) (III), \(\text{mer-}[\text{Re(CS)(Me}_2\text{PhP)}_3(\text{Et}_2\text{dtc})]\) and
\((\text{diethyldithiocarbamato})\text{thiocarbonyl}]\) (III), [\(\text{Re(CS)(Et}_2\text{dtc)}_3\)] have been studied by
infrared and NMR spectroscopy, mass spectrometry and X-ray diffraction.

\(\text{mer-}[\text{Re(CS)(Me}_2\text{PhP)}_3(\text{Et}_2\text{dtc})]\) crystallizes orthorhombic in the space group \(Pn\alpha_2\), with
\(a = 1516.1(2), b = 2189.8(2)\) and \(c = 1035.6(1)\) pm. Structure solution and refinement converged at \(R = 0.042\). The coordination geometry is a distorted octahedron. The \(\text{Re-C}\) bond length is found to be 184(2) pm.

\([\text{Re(CS)(Et}_2\text{dtc)}_3]\) crystallizes monoclinic in the space group \(P2_1/c\) with \(a = 962.2(6), b = 1744.0(2), c = 1537.4(6)\) pm and \(\beta = 96.21(1)^\circ\). The final \(R\) value is 0.028. In the monomeric complex the rhenium atom is seven-coordinate with an approximate pentagonal-bipiramidal coordination sphere and a rhenium-carbon distance of 181(1) pm.

Although a stable molecular CS does not exist, a number of thiocarbonyl complexes have been synthe­nized and studied by various spectroscopic methods [1]. Thiocarbonyl ligands have been found as terminal as well as bridging moieties in transition metal complexes. The most important procedure to generate CS complexes is the use of \(\text{CS}_2\) or its complexes. Additionally, reactions are found under an atmosphere of dry nitrogen.

Routine infrared spectra were recorded as KBr discs on a SPECORD 75 IR. NMR spectra were obtained in CDC\textsubscript{13} solutions on a 
BRUKER AMX-400 spectrometer with TMS and phosphoric acid as internal standards. FAB mass spectra were recorded on a MAT 701A spectrometer (FINNIGAN). Xenon was used as primary beam gas. The ion gun was operated at 8 kV and 100 \(\mu\)A (probe temperature: 30 °C). Nitrobenzaldehyde was used as matrix.

X-ray data were collected on an Enraf-Nonius CAD4 diffractometer. The structures of \([\text{Re(CS)(Me}_2\text{PhP)}_3(\text{Et}_2\text{dtc})]\) and \([\text{Re(CS)(Et}_2\text{dtc)}_3]\) were solved by the Patterson method. All non-hydrogen atoms were located from successive Fourier maps. The hydrogen atoms were placed at

**Experimental**

\([\text{ReCl}_3(\text{Me}_2\text{PhP)}_3]\) was prepared following a literature procedure [10]. All reactions were performed under an atmosphere of dry nitrogen.

**Abbreviations used:** 
- \(\text{Me}_2\text{PhP}\) = dimethylphenylphosphine
- \(\text{Et}_2\text{dtc}\) = diethyldithiocarbamatoanion

* Reprint requests to Dr. U. Abram.

Verlag der Zeitschrift für Naturforschung,
D-W-7400 Tübingen
0932-0776/93/0600-0771/5 01.00/0

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.
calculated positions and included in the structure-factor calculations. Crystal data and details of the refinements are summarized in Table I*. Positional parameters are given in Tables II and III.

\[ \text{Re(CS)(Me}_2\text{PhP)}_3(\text{Et}_2\text{dtc}) \]

707 mg (1 mmol) [ReCl₃(Me₂PhP)₃] were dissolved in about 300 ml ethanol. 675 mg (3 mmol) NaEt₂dtc·3H₂O were added in 100 ml ethanol, and the mixture was refluxed for 2.5 h. After reducing the volume of the dark red reaction mixture to 150 ml and standing overnight at ambient temperature yellow crystals deposited which were collected by filtration and washed with cold ethanol and water to remove excess NaEt₂dtc and sodium chloride. The product was recrystallized from CH₂Cl₂/hexane or diethylether/hexane to give bright yellow needles. Yield: 350 mg (45% based on Re).

The yield can be increased by further evaporation of the mother liquor. This product, however, is contaminated with [Re(CS)(Et₂dtc)₃] and [ReO(Et₂dtc)₃]O, which are formed as by-products.

FAB mass spectrum: \( m/z = 793 \) [Re(CS)(Me₂PhP)₃(Et₂dtc)]⁺ (M⁺), 655 [M–Me₂PhP]⁺, 517 [M–2Me₂PhP]⁺, 379 [M–3Me₂PhP]⁺.

NMR spectra: \(^1\)H NMR: CH₃ (dithiocarbamate) 1.28 ppm tr. (3H) and 1.39 ppm tr. (3H); CH₃ (cis-Me₂PhP) 1.56 ppm d. (broad) (6H); CH₃ (trans-Me₂PhP) 1.92 ppm s. (broad) (6H) and 2.05 ppm s. (broad) (6H); CH₃ 3.65 ppm qu. (2H) and 3.77 ppm qu. (2H); phenyl 7.15–7.80 ppm m. (15H). – \(^{13}\)C NMR: CH₃ (dithiocarbamate) 12.75 ppm and 12.98 ppm; CH₃ (cis-Me₂PhP) 19.16 ppm d. (JPC = 32 Hz); CH₃ (trans-Me₂PhP) AX' spectrum 12.19 and 17.25 ppm tr. (N = 28 Hz); CH₃ 43.54 and 44.11 ppm; phenyl 127.77, 127.96, 128.10, 128.97, 130.55, 143.03, 146.35 and 146.76 ppm; C–N 211.57 ppm, C=S 277.82 ppm. – \(^{31}\)P NMR: cis-Me₂PhP -18.67 ppm; trans-Me₂PhP 35.89 ppm.

Infrared spectrum: C=S 1178 cm⁻¹ (s).

C₃₀H₄₃N₃P₃S₃Re (793)
Calcd C 45.4 H 5.4 N 1.8 S 12.1%.
Found C 45.2 H 5.6 N 1.7 S 11.9%.

\[ \text{Re(CS)(Me}_2\text{PhP)}_3(\text{Et}_2\text{dtc}) \]

707 mg (1 mmol) [ReCl₃(Me₂PhP)₃] were dissolved in about 300 ml ethanol. 1.125 g (5 mmol) NaEt₂dtc·3H₂O were added in 100 ml ethanol.

Table I. Crystal data collection and structure refinement parameters.
Table II. Fractional positional parameters* for [Re(CS)(Me2PhP)3(Et2dtc)].

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re1</td>
<td>0.21255(3)</td>
<td>0.07135(2)</td>
<td>2.000(5)</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>0.1059(3)</td>
<td>0.1818(2)</td>
<td>1.784(5)</td>
<td>3.93(9)</td>
</tr>
<tr>
<td>S2</td>
<td>0.1133(2)</td>
<td>-0.0184(2)</td>
<td>0.0324(4)</td>
<td>2.54(7)</td>
</tr>
<tr>
<td>S3</td>
<td>0.2681(2)</td>
<td>-0.0218(2)</td>
<td>-0.1304(2)</td>
<td>2.54(7)</td>
</tr>
<tr>
<td>P1</td>
<td>0.1134(3)</td>
<td>0.0966(2)</td>
<td>-0.1736(5)</td>
<td>2.97(8)</td>
</tr>
<tr>
<td>P2</td>
<td>0.3300(3)</td>
<td>0.1338(2)</td>
<td>-0.0698(4)</td>
<td>2.50(8)</td>
</tr>
<tr>
<td>P3</td>
<td>0.2813(3)</td>
<td>0.0351(2)</td>
<td>0.1932(4)</td>
<td>2.49(7)</td>
</tr>
<tr>
<td>N1</td>
<td>0.1580(9)</td>
<td>-0.1191(6)</td>
<td>-0.1021(2)</td>
<td>3.48(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.157(1)</td>
<td>0.1310(7)</td>
<td>0.096(2)</td>
<td>2.7(3)</td>
</tr>
<tr>
<td>C2</td>
<td>0.177(1)</td>
<td>-0.0616(7)</td>
<td>-0.072(2)</td>
<td>2.6(3)</td>
</tr>
<tr>
<td>C3</td>
<td>0.211(1)</td>
<td>-0.1520(8)</td>
<td>-0.0199(2)</td>
<td>3.94(4)</td>
</tr>
<tr>
<td>C4</td>
<td>0.166(1)</td>
<td>-0.146(1)</td>
<td>-0.330(2)</td>
<td>5.4(5)</td>
</tr>
<tr>
<td>C5</td>
<td>0.059(1)</td>
<td>-0.1050(8)</td>
<td>-0.044(2)</td>
<td>4.2(4)</td>
</tr>
<tr>
<td>C6</td>
<td>0.108(1)</td>
<td>-0.1799(8)</td>
<td>0.085(2)</td>
<td>3.94(4)</td>
</tr>
<tr>
<td>C7</td>
<td>0.153(1)</td>
<td>-0.0782(8)</td>
<td>0.096(2)</td>
<td>2.7(3)</td>
</tr>
<tr>
<td>C8</td>
<td>0.0275(8)</td>
<td>0.0490(5)</td>
<td>0.298(5)</td>
<td>4.5(2)</td>
</tr>
<tr>
<td>C9</td>
<td>0.075(1)</td>
<td>0.1280(8)</td>
<td>0.345(8)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>C10</td>
<td>0.065(1)</td>
<td>0.1580(8)</td>
<td>0.308(8)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>C11</td>
<td>0.154(1)</td>
<td>0.2250(8)</td>
<td>0.368(8)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>C12</td>
<td>0.062(1)</td>
<td>0.1170(8)</td>
<td>0.286(8)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>C13</td>
<td>0.165(1)</td>
<td>0.1200(8)</td>
<td>0.321(8)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>C14</td>
<td>0.231(1)</td>
<td>-0.0572(8)</td>
<td>0.223(8)</td>
<td>8.3(3)</td>
</tr>
<tr>
<td>C15</td>
<td>0.1397(6)</td>
<td>0.1475(4)</td>
<td>0.2168(4)</td>
<td>2.6(3)</td>
</tr>
<tr>
<td>C16</td>
<td>0.0967(6)</td>
<td>0.1687(4)</td>
<td>0.2031(4)</td>
<td>2.6(3)</td>
</tr>
<tr>
<td>C17</td>
<td>0.0967(6)</td>
<td>0.1687(4)</td>
<td>0.2031(4)</td>
<td>2.6(3)</td>
</tr>
<tr>
<td>C18</td>
<td>0.0967(6)</td>
<td>0.1687(4)</td>
<td>0.2031(4)</td>
<td>2.6(3)</td>
</tr>
</tbody>
</table>

* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \( B = \frac{4}{3} \left( a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + a b \cos \beta B_{12} + a c \cos \gamma B_{13} + b c \cos \alpha B_{23} \right) \) (in \( \text{Å}^2 \)).

Results and Discussion

and the mixture was refluxed for 12 h. After reducing the volume of the reaction mixture to about 100 ml and standing overnight in a refrigerator red crystals deposited which were collected by filtration, washed successively with ethanol, water, ethanol and diethyl ether. The product was recrystallized from CHCl3/methanol to give dark red blocks. Yield: 440 mg (65% based on Re).

FAB mass spectrum: \( m/z = 675 \) \([\text{Re(CS)(Et2dtc)}]^{+}\) (M+), 631 \([\text{M-CS]}^{+}\), 599 \([\text{M-CS-}]^{+}\), 527 \([\text{Re(CS)(Et2dtc)}]^{-}\), 483 \([\text{Re(Et2dtc)}]^{+}\), 399 \([\text{ReS2(Et2dtc)}]^{+}\), 367 \([\text{Re(S2Et2dtc)}]^{+}\), 335 \([\text{Re(Et2dtc)}]^{+}\).

Table III. Fractional positional parameters* for [Re(CS)(Et2dtc)].

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re1</td>
<td>0.19523(3)</td>
<td>0.08709(2)</td>
<td>0.21661(2)</td>
<td>2.364(4)</td>
</tr>
<tr>
<td>S1</td>
<td>0.1167(2)</td>
<td>-0.0130(1)</td>
<td>0.1085(1)</td>
<td>3.19(3)</td>
</tr>
<tr>
<td>S2</td>
<td>0.0310(2)</td>
<td>0.0292(1)</td>
<td>0.2469(1)</td>
<td>3.01(3)</td>
</tr>
<tr>
<td>S3</td>
<td>0.3680(2)</td>
<td>0.0768(1)</td>
<td>0.1085(1)</td>
<td>3.67(4)</td>
</tr>
<tr>
<td>S4</td>
<td>0.4108(2)</td>
<td>0.1609(1)</td>
<td>0.2630(1)</td>
<td>3.34(4)</td>
</tr>
<tr>
<td>S5</td>
<td>0.1721(2)</td>
<td>0.3742(1)</td>
<td>0.8652(1)</td>
<td>2.83(3)</td>
</tr>
<tr>
<td>S6</td>
<td>0.3054(2)</td>
<td>-0.0161(1)</td>
<td>0.3245(1)</td>
<td>2.96(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.1080(7)</td>
<td>0.3297(4)</td>
<td>0.6656(4)</td>
<td>2.8(1)</td>
</tr>
<tr>
<td>C2</td>
<td>0.1674(7)</td>
<td>0.3767(4)</td>
<td>0.6043(4)</td>
<td>2.8(1)</td>
</tr>
<tr>
<td>C3</td>
<td>0.3703(7)</td>
<td>0.1468(4)</td>
<td>0.2931(4)</td>
<td>2.8(1)</td>
</tr>
<tr>
<td>C4</td>
<td>0.1087(7)</td>
<td>0.3791(4)</td>
<td>0.6043(4)</td>
<td>2.8(1)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0331(7)</td>
<td>0.1468(4)</td>
<td>0.2931(4)</td>
<td>2.8(1)</td>
</tr>
<tr>
<td>C6</td>
<td>0.1477(7)</td>
<td>0.3791(4)</td>
<td>0.6043(4)</td>
<td>2.8(1)</td>
</tr>
</tbody>
</table>

* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: \( B = \frac{4}{3} \left( a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + a b \cos \beta B_{12} + a c \cos \gamma B_{13} + b c \cos \alpha B_{23} \right) \) (in \( \text{Å}^2 \)).

NMR spectra: \(^1H\) NMR: CH3 1.24 ppm tr. (3H), CH3 3.52 ppm qu. (2H). \(^13C\) NMR: CH3 12.74 ppm, CH3 43.33 ppm, C-N 203.48 ppm, C=S 271.73 ppm.

Infrared spectrum: C=S 1234 cm\(^{-1}\) (s).

\[\text{C}_6\text{H}_{16}\text{N}_2\text{S-Re (675)}\]
Calcd C 28.4 H 4.4 N 6.2 S 33.2%
Found C 28.2 H 4.9 N 6.0 S 33.5%

Results and Discussion

[Re(CS)(Me2PhP)3(Et2dtc)] and [Re(CS)(Et2dtc)] are novel rhenium complexes with terminal thiocarbonyl ligands. They can be obtained by a very facile procedure from [ReCl3(Me2PhP)] and sodium diethylthiocarbamate in ethanol solution. A similar reaction could not be observed using acetone as solvent. This result is in accordance with the report of Rowbottom and Wilkinson who
isolated the neutral, paramagnetic tris-chelate [Re(ETdtc)3] as red-brown needles from the reaction of [ReCl3(Ph3P)2(AN)] (AN = acetonitrile) and sodium diethylthiocarbamate in acetone [18]. The preferred formation of [Re(CS)(ETdtc)3] during longer reaction periods cannot be explained as a simple, secondary ligand exchange reaction starting from the primary product [Re(CS)(Me2PhP)3(ETdtc)]. This reaction leads to the well-known oxo-bridged rhenium(V) complex [ReO(ETdtc)2]O which was also obtained as a by-product during the [Re(CS)(Me2PhP)3(ETdtc)] synthesis.

The formation of thiocarbonyl ligands from organic ligands which contain CS groups is not very common, but has been observed previously, e.g. during the reaction of [Fe(cp)(CO)2]+ (cp = cyclopentadienyl anion) with ethylchlorothioformiate [11, 12]. For dithiocarbamates, however, there is no precedent. The formation of the terminal CS ligand probably results from the decomposition of an intermediate complex with an η2-CS bonded dithiocarbamate and the formal loss of NaNEt₂. The formation of Me₂PhPS may be responsible for the abstraction of one sulphur atom. The low yields which were obtained for the synthesis of [ReO(ETdtc)2]O (less than 50 per cent) confirm this assumption. Unfortunately, all attempts to isolate an intermediate of the reaction failed up to now.

The title compounds are stable in air both as solids as well as in solution. They are readily soluble in organic solvents such as chloroform, benzene or acetone ([Re(CS)(Me2PhP)3(ETdtc)] shows also a good solubility in diethylether), and moderately soluble in alcohols.

Strong infrared bands are observed at 1178 cm⁻¹ for [Re(CS)(Me2PhP)3(ETdtc)] and at 1234 cm⁻¹ for [Re(CS)(ETdtc)3] which can be assigned to the CS stretching vibrations. These bands are in the typical range of ν(CS) vibrations in thiocarbonyl complexes with σ-bonded CS ligands [1].

Both complexes are diamagnetic as expected for the d⁶-configuration of [Re(CS)(Me2PhP)3(ETdtc)] and a seven coordinate rhenium(III) compound [13]. ¹H and ¹³C NMR spectra of [Re(CS)(ETdtc)3] confirm that all three dithiocarbamate ligands are magnetically equivalent. The spectra of [Re(CS)(Me2PhP)3(ETdtc)] show typical high order patterns due to diastereotopic methyl groups in the Me₂PhP ligands and couplings with the ³¹P nuclei. The coupling pattern in the ¹³C spectrum has been studied with the DEPT 135 technique, which gives two signals for the CH₃ and CH₂ protons of the diethylthiocarbamate ligand. Obviously rotation about the C–N bond is hindered in [Re(CS)(Me₂PhP)₃(ETdtc)]. This is in contrast to the results for [Re(CS)(ETdtc)3] and may be explained by the sterical influence of the meridionally coordinated Me₂PhP ligands. In the ³¹P spectrum of [Re(CS)(Me₂PhP)₃(ETdtc)] only two signals could be observed indicating equivalence of the trans-coordinated phosphines. In the ¹³C NMR spectra of the CS carbon atoms can be observed at 277.8 ppm ([Re(CS)(Me₂PhP)₃(ETdtc)]) and 271.7 ppm ([Re(CS)(ETdtc)3]), respectively. Both values are amongst the least downfield shifted ¹³C NMR signals which have been observed for terminal CS ligands (the typical range is between 280 and 390 ppm [1]).

Fast atom bombardment mass spectrometry has been used to study the fragmentation pattern of the new thiocarbonyl complexes. The spectra are characterized by intense peaks due to the molecular ions. Fig.1 shows the spectrum of [Re(CS)(Me₂PhP)₃(ETdtc)]. Abstraction of CS during the mass spectrometric fragmentation could only be observed with [Re(CS)(ETdtc)3]. This can be understood as due to the chelating power of the dithiocarbamate ligand and the sta-
bility of the [Re(Et₂dtc)₃] moiety [18]. The fragmentation of [Re(CS)(Me₂PhP)₃(Et₂dtc)] mainly occurs by loss of complete Me₂PhP ligands. Peaks at m/z = 671 and m/z = 533 are due to the formation of phosphine oxide complexes by partial oxidation of phosphine ligands in the FAB matrix and has been observed previously during mass spectrometric studies on technetium phosphate complexes [14, 15].

Crystals of [Re(CS)(Me₂PhP)₃(Et₂dtc)] suitable for X-ray diffraction could be obtained by slow evaporation of a diethylether/n-hexane solution. The structure consists of monomeric [Re(CS)(Me₂PhP)₃(Et₂dtc)] molecules. A SCHAKAL plot [16] is given in Fig. 2. Table IV contains selected interatomic distances and angles. The rhenium atom is six-coordinate with the three phosphine ligands coordinated meridionally cis to the thiocarbonyl group. The complex is markedly distorted from the octahedral geometry, with the S² atom bent out of the equatorial plane formed by the three phosphorus atoms by 84.8(4) pm, away from the thiocarbonyl, probably owing to the small bite of the dithiocarbamate ligand (S²-C₂-S₃ 112.7(8)°), which also explains the C₁-Re-S₃ angle of 171.1(6)°. The ReCS unit is nearly linear with a Re-C₁ distance of 184(2) pm which is in the normal range for metal-thiocarbonyl bonds [1]. The relatively long C₁-S₁ bond length of 160(2) pm suggests significant π-accepting properties of the CS ligand. This is confirmed by a marked structural trans effect of the thiocarbonyl group which can be derived from the lengthening of the Re-S₃ bond in comparison with the Re-S₂ distance by 9 pm.

[Re(CS)(Et₂dtc)₃] crystallizes from a dichloromethane/methanol mixture in form of large red blocks suitable for an X-ray structure determination. The complex is monomeric with the rhenium atom in a seven-coordinate environment. A plot of the structure along with the atomic numbering scheme is given in Fig. 3. Selected bond lengths and angles are summarized in Table V. The coordination geometry is best described as a distorted pentagonal bipyramid with the thiocarbonyl group occupying one axial position. Two dithiocarbamate ligands are equatorially coordinated as is the sulphur atom S₅ of the third Et₂dtc ligand, while S₆ occupies the second axial position. The bonding situation is thus fully consistent with that in the analogous carbonyl complex [Re(CO)(Et₂dtc)₃] [17]. The atoms S₁-S₄ are nearly coplanar, but S₅ deviates from this plane due to the small bite of the Et₂dtc ligand, which is also the reason for the S₆-Re-C₁₀ angle of 166.0(2)°. The Re-C₁₀ distance of 181.1(7) pm

Table IV. Selected bond lengths and angles in [Re(CS)(Me₂PhP)₃(Et₂dtc)] along with esd's.

| Bond lengths [pm]          |     |
|---------------------------|--|--|
| Re-C₁ 184(2)              | Re-P₂ 235.2(4) | S₂-C₂ 173(2) |
| Re-S₂ 249.1(4)            | Re-P₃ 238.6(5) | S₃-C₂ 173(2) |
| Re-S₃ 258.0(5)            | S₁-C₁ 160(2)  | C₂-N₁ 133(3) |
| Re-P₁ 240.0(5)            |     |     |

| Bond angles [°]            |     |
|---------------------------|--|--|
| S₂-Re-S₃ 69.2(1)           | P₁-Re-P₂ 96.2(2) |
| S₂-Re-P₁ 84.6(1)           | P₁-Re-C₁ 87.6(6) |
| S₂-Re-P₂ 162.2(1)          | P₂-Re-P₃ 96.9(1) |
| S₂-Re-P₃ 83.6(1)           | P₂-Re-C₁ 95.7(6) |
| S₂-Re-C₁ 102.1(5)          | P₃-Re-P₁ 88.9(6) |
| S₃-Re-P₁ 89.7(1)           | P₃-Re-C₁ 89.6(5) |
| S₃-Re-P₂ 93.0(1)           | Re-S₂-C₂ 90.5(5) |
| S₃-Re-P₃ 91.9(1)           | Re-S₃-C₂ 87.6(5) |
| S₃-Re-C₁ 171.1(6)          | Re-C₁-S₁ 178.1(9) |

Fig. 2. SCHAKAL [16] plot of [Re(CS)(Me₂PhP)₃(Et₂dtc)] with the atomic numbering scheme.
Table V. Selected bond lengths and angles in [Re(CS)(Et$_2$dtc)$_3$] along with esd's.

<table>
<thead>
<tr>
<th>Bond lengths [Å]</th>
<th>Bond angles [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-C10 181.1(7) Re-S6 259.4(2) S5-C21 173.2(7)</td>
<td>S1-Re-S2 68.23(6) S4-Re-S6 84.54(6)</td>
</tr>
<tr>
<td>Re-S1 247.1(2) S10-C10 159.8(7) S6-C21 172.0(8)</td>
<td>S1-Re-S3 71.13(6) S4-Re-C10 92.5(2)</td>
</tr>
<tr>
<td>Re-S2 248.8(2) S1-C1 170.3(7) N1-C1 131.3(9)</td>
<td>S1-Re-S4 138.20(7) S5-Re-S6 70.28(6)</td>
</tr>
<tr>
<td>Re-S3 248.1(3) S2-C1 171.9(7) N2-C11 132(1)</td>
<td>S1-Re-S5 141.33(6) S5-Re-C10 95.7(2)</td>
</tr>
<tr>
<td>Re-S4 247.9(2) S3-C11 169.1(7) N3-C21 130.4(7)</td>
<td>S1-Re-S6 90.80(6) S6-Re-C10 166.0(2)</td>
</tr>
<tr>
<td>Re-S5 241.6(2) S4-C11 173.2(7)</td>
<td>S1-Re-C10 100.5(3) Re-S1-C1 91.9(2)</td>
</tr>
<tr>
<td>Bond angles [°]</td>
<td></td>
</tr>
<tr>
<td>S1-Re-S2 68.23(6) S4-Re-S6 84.54(6)</td>
<td>S1-Re-S3 71.13(6) S4-Re-C10 92.5(2)</td>
</tr>
<tr>
<td>S1-Re-S4 138.20(7) S5-Re-S6 70.28(6)</td>
<td>S1-Re-S5 141.33(6) S5-Re-C10 95.7(2)</td>
</tr>
<tr>
<td>S1-Re-S6 90.80(6) S6-Re-C10 166.0(2)</td>
<td>S1-Re-C10 100.5(3) Re-S1-C1 91.9(2)</td>
</tr>
<tr>
<td>S2-Re-S3 139.36(6) Re-S2-C1 90.9(2)</td>
<td>S2-Re-S4 151.44(6) Re-S3-C11 91.9(3)</td>
</tr>
<tr>
<td>S2-Re-S5 76.39(6) Re-S4-C11 91.0(2)</td>
<td>S2-Re-S6 84.51(6) Re-S5-C21 90.9(2)</td>
</tr>
<tr>
<td>S2-Re-C10 91.8(2) Re-S6-C21 85.4(2)</td>
<td>S2-Re-C10 91.8(2) Re-S6-C21 85.4(2)</td>
</tr>
<tr>
<td>S3-Re-S4 68.28(6) Re-C10-S10 176.0(4)</td>
<td>S3-Re-S5 142.26(7) S1-C1-S2 108.7(4)</td>
</tr>
<tr>
<td>S3-Re-S5 142.26(7) S1-C1-S2 108.7(4)</td>
<td>S3-Re-S6 96.94(6) S3-C11-S4 108.8(5)</td>
</tr>
<tr>
<td>S3-Re-C10 94.6(2) S5-C21-S6 113.5(4)</td>
<td>S4-Re-S5 75.09(6)</td>
</tr>
</tbody>
</table>

Fig. 3. SCHAKAL [16] plot of [Re(CS)(Et$_2$dtc)$_3$] with the atomic numbering scheme.

is shorter by 5 pm in comparison to that in [Re(CO)(Et$_2$dtc)$_3$] [17], which seems to be a general tendency in pairs of carbonyl/thiocarbonyl complexes [1] indicating that the M–CS interaction is stronger. There are no significant differences in the bonding of the CS groups in [Re(CS)(Et$_2$dtc)$_3$] and [Re(CS)(Me$_2$PhP)$_3$(Et$_2$dtc)]. The Re–S(axial) bonds are longer than the equatorial bonds due to the trans-labilizing influence of the CS ligand. Interestingly, the Re–S5 distance in [Re(CS)(Et$_2$dtc)$_3$] (241.6(2) pm) is markedly shorter than the other equatorial Re–S bonds in both compounds (247.1(2)–249.1(4) pm).

With [Re(CS)(Me$_2$PhP)$_3$(Et$_2$dtc)] and [Re(CS)(Et$_2$dtc)$_3$] two compounds have been synthesized and characterized which have considerable potential as starting materials for the synthesis of other rhenium thiocarbonyl complexes and/or products of nucleophilic or electrophilic attacks [1] at the CS ligands. Efforts to synthesize and characterize such compounds are in progress.

We would like to acknowledge grants from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, and express our thanks to Professor J. Strähle (Tübingen) for his hospitality and for providing us with facilities. We also thank Dr. H. Mayer (Tübingen) for valuable help in the interpretation of the NMR spectra.
Coordination and Reactions of Diazenes in Trimethylphosphinecobalt(I) Complexes – Syntheses and Structures of Complexes Containing $\mu^2-(N,N')$-Benzo[c]cinnoline and $\eta^2$-Azobenzene Ligands

Hans-Friedrich Klein* a, Michael Helwig a, Udo Koch a, Ulrich Flörke b, and Hans-Jürgen Haupt b

a Eduard-Zintl-Institut für Anorganische Chemie der Technischen Hochschule Darmstadt, Hochschulstraße 10, D-W-6100 Darmstadt
b Anorganische und Analytische Chemie der Universität/GH Paderborn, Warburger Straße 100, D-W-4790 Paderborn

Z. Naturforsch. 48b, 778–784 (1993); received October 23, 1992

Azobenzene, Benzo[c]cinnoline, Cobalt(I) Complexes, Synthesis, Crystal Structure

Introduction

Continuing our studies of diazene coordination and reactions in low-valent cobalt complexes we wished to compare paramagnetic metal $d^9$ compounds of cobalt(0) [1] with $d^8$ complexes of cobalt(I) and cis-fixed benzo[c]cinnoline with trans-azobenzene ligands. Only trans aryl diazenes adopt conformations suitable for ortho-metallation reactions [2] that can be envisaged to proceed according to eqs (1) or (2).

While with diazene compounds of cobalt(0) only the first step of eq. (1) was observed, for cobalt(I) a series of leaving groups are available promoting reaction according to eq. (2): $R = \text{CH}_3$, $\text{C}_6\text{H}_5$, $\text{C} \equiv \text{CR}'$ ($R' = \text{alkyl, aryl}$).

Benzo[c]cinnoline cannot form a five-membered chelate ring and is therefore expected to activate either $\sigma(N)$ or $\pi(N,N')$ donor functions for coordination in mononuclear or dinuclear cobalt(I) compounds. For carbonyl-free complexes it was of interest to obtain structural information on the coordination mode of the diazene adopted in the absence of bridge-forming ligands.

Experimental

General procedures and materials

Details of experimental techniques and analytical methods have been given elsewhere [1]. 4-Acetoxy-azobenzene was prepared from 4-hydroxy-azobenzene (Merck-Schuchardt). Published procedures were used for $\text{CpCo}(\text{PMe}_3)_2$ [3], $\text{CoCH}_3(\text{PMe}_3)_4$ [4], $\text{CoC}_6\text{H}_5(\text{PMe}_3)_4$ [5] $\text{CoC} \equiv \text{CC}_6\text{H}_5(\text{PMe}_3)_4$ [4].

Preparations

$\eta^2$-Cyclopentadienyl-($\eta^2-N,N'$-azobenzene)-(trimethylphosphine)cobalt (1)

400 mg $\text{Co}(\text{C}_5\text{H}_5)(\text{PMe}_3)_2$ (1.45 mmol) and 260 mg of azobenzene (1.43 mmol) in 30 ml of
THF are kept at 20 °C. After 18 h the volatiles are removed in vacuo and the brown residue is extracted with 60 ml pentane over a glass sinter-disc (G 3). Over dry-ice 240 mg of dark blue cubic crystals are obtained. Evaporating the mother liquor to 30 ml and cooling over dry-ice gives another crop of 150 mg. Total yield 390 mg (71% based on azobenzene), m. p. 114–115 °C.

Analysis for $C_{20}H_{24}CoN_2P_3$ (382.3)
Calcd C 62.83 H 6.33 N 7.33 P 8.10%.
Found C 63.18 H 6.45 N 7.51 P 8.37%.

1H NMR (300 MHz, toluene-d$_8$, 298 K, Me$_4$Si external reference): $\delta$CH$_3$ 0.73 (d, 9H, $^3$(PH) 9.8 Hz), $\delta$C$_6$H$_5$ 4.46 (s, 5H), $\delta$C$_6$H$_4$(2-H) 7.96 (d, 2H, $^3$(PH) 7.3 Hz), $\delta$C$_6$H$_4$(3,4-H) 7.3–8.6 (m, 3H, interference with toluene resonance). $^13$C NMR (75.4 MHz, toluene-d$_8$, 193 K, H$_3$PO$_4$ external standard): $\delta$PCH$_3$ 19.4 (t, $^3$(PC) + $^3$(PH) 26.4 Hz), $\delta$CCH$_3$ 85.0 s, $\delta$C$_6$H$_5$ 125.3 s, 128.7 s, 129.3 s.

2-Phenyldiazenido-phenyl($\eta^2$-C,N')-tris(trimethylphosphine) cobalt (2)
1230 mg CoMe(PMe$_3$)$_3$ (3.25 mmol) in 90 ml of pentane at −60 °C are combined with 590 mg of azobenzene (3.25 mmol) to form a red solution under evolution of gas. After 1 h at 20 °C the volume is reduced to 25 ml in vacuo. A dark precipitate is isolated by decantation and dissolved in 20 ml of ether. At −25 °C dark red crystals are obtained that are dried in vacuo. Yield 1390 mg (91%), m. p. 113–115 °C.

Analysis for $C_{19}H_{38}CoN_2P_3$ (268.4)
Calcd C 54.29 H 6.47 N 6.66%.
Found C 54.36 H 6.47 N 6.64%.

1H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta$PCH$_3$ 0.62 (t, 18H, $^3$(PH) 9.0 Hz), $\delta$CH$_3$ 0.91 (d, 9H, $^3$(PH) 6.7 Hz), $\delta$C$_6$H$_5$ 6.7–8.7 (m, 9H). $^13$C NMR (121.5 MHz, C$_6$D$_6$, 193 K, H$_3$PO$_4$ external standard): $\delta$PCH$_3$ 1.21 (m, 3H, $^3$(PC) 0.25 (t, 18H, $^3$(PH) 9.0 Hz), $\delta$CH$_3$ 1.21 (m, 18H), 1.34 (d, 9H, $^3$(PH) 6.7 Hz), $\delta$C$_6$H$_5$ 7.6–8.7 (m, 18H).

2-Phenyldiazenido-4-acetoxy-phenyl-tris(trimethylphosphine) cobalt (3a)
2-[(4-acetoxyphenyl-diazenido)phenyl]tris(trimethylphosphine) cobalt (3b)
1310 mg CoMe(PMe$_3$)$_3$ (3.46 mmol) and 770 mg of 4-acetoxyazobenzene (3.46 mmol) in 60 ml of ether are kept at 0 °C for 20 min and at 20 °C for 3 h. Reducing the volume to 20 ml in vacuo and cooling over dry-ice affords a microcrystalline red solid. Yield 1440 mg (79%).

Analysis for $C_{23}H_{38}CoN_2O_3P_3$ (526.4)
Calcd C 52.48 H 7.28 N 5.32%.
Found C 52.05 H 7.03 N 5.14%.

IR (Nujol mull, 2600–1600 cm$^{-1}$): 1918 vs vCO.

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta$PCH$_3$ 0.84 (s, 54H), $\delta$COCH$_3$ 1.80 (s, 3H), 1.92 (s, 3H), $\delta$CH$_3$ 6.97 (m, 3H), 7.12 (m, 4H), 7.32 (m, 4H), 7.48 (t, 1H, $^3$(HH) 7.1 Hz), 8.16 (m, 1H), 8.23 (d, 1H, $^3$(HH) 6.5 Hz), 8.52 (d, 1H, $^3$(HH) 7.5 Hz), 8.62 (d, 1H, $^3$(HH) 6.7 Hz).

$^13$C NMR (75.4 MHz, C$_6$D$_6$, 298 K): $\delta$COCH$_3$ 20.6 s, 21.2 s, $\delta$PCH$_3$ 16.5 m, $\delta$C$_6$H$_5$ 116.2 s, 117.5 s, 120.4 s, 120.6 s, 122.8 s, 125.0 s, 126.2 s, 126.7 s, 126.9 s, 145.2 s, 162.0 s, 162.4 s, 168.7 s.

2-Phenyldiazenido-phenyl($\eta^2$-C,N')-carbonyl-bis(trimethylphosphine) cobalt (4)
850 mg 2 (1.18 mmol) in 30 ml of THF under 1 bar CO are kept stirring for 20 min. The volatiles are removed in vacuo and the residue is crystallized from ether at −10 °C to give violet-red cubes. Yield 670 mg (88%), m. p. 113–114 °C.

Analysis for $C_{24}H_{36}CoN_2O_2P_2$ (420.3)
Calcd C 54.29 H 6.47 N 6.66%.
Found C 54.36 H 6.47 N 6.64%.

Methyl($\eta^2$-N,N'-benzo[c]cinnoline)-tris(trimethylphosphine) cobalt (5)
620 mg CoMe(PMe$_3$)$_3$ (1.64 mmol) and 290 mg of benzo[c]cinnoline (1.61 mmol) in 60 ml of THF on warming from −70 °C to 20 °C form a violet solution. After 3 h the volatiles are removed in vacuo and the residue is extracted with 60 ml THF/pentane (2:1). After two weeks at −70 °C violet plates are obtained. Yield 270 mg (34%), decomp. >80 °C.

Analysis for $C_{24}H_{38}CoN_2P_3$ (482.4)
Calcd C 54.78 H 7.94 N 5.81%.
Found C 54.76 H 7.67 N 5.83%.

Methyl($\mu^2$-N,N'-benzo[c]cinnoline-bis(cyclopentadienyl))-trimethylphosphine-dicobalt (6)
680 mg CoCp(PMe$_3$)$_2$ (2.46 mmol) and 440 mg of benzo[c]cinnoline (2.44 mmol) in 50 ml of THF
on warming from -70 °C to 20 °C turn from brown to red-violet. The volatiles are removed in vacuo and the residue is dissolved in 50 ml of fresh THF. After 48 h the solution is evaporated to dryness and the residue extracted with pentane. Over dry-ice a crystalline material is obtained that is re-crystallized from 40 ml of pentane/ether (1:1) at -30 °C. After 3 d dark green shining crystals are obtained. Yield 140 mg (23% based on cobalt), decomp. >135 °C.

**Analysis for C$_2$H$_7$Co$_2$N$_2$P (504.3)**

Calcd C 59.54 H 5.40 N 5.55%,

Found C 58.66 H 5.41 N 5.76%.

$^1$H NMR (300 MHz, THF-d$_8$, 298 K): $^3$PCH$_3$ 1.60 (d, 9H, $^2$J(PPH) 9.3 Hz), $^3$C$_5$H$_5$ 4.75 (s, 10H), $^3$C$_6$H$_5$N$_2$ 6.75 (m, 2H), 6.95 (dd, 2H, $^3$J(HH) 7.5 Hz, $^3$J(HH) 1.0 Hz), 8.08 (t, 2H, $^3$J(HH) 8.4 Hz). $^{-13}$C NMR (75.4 MHz, THF-d$_8$, 298 K): $^3$PCH$_3$ 20.9 (d, $^1$J(HC) 28.6 Hz), $^3$C$_5$H$_5$ 76.6 s, $^3$C$_6$H$_5$N$_2$ 112.6 s, 116.1 s, 125.9 s, 134.8 s.

**X-ray data collection and structure solution**

**Complex 1:** C$_{20}$H$_{24}$Co$_2$N$_2$P (382.3). A dark blue specimen (0.21 $\times$ 0.31 $\times$ 0.36 mm) was sealed under argon into a glass capillary and mounted on a Nicolet R3m/V diffractometer. Using graphite-monochromated MoK$_{\alpha}$-radiation lattice parameters were obtained from 30 reflections with 10 $\leq \theta \leq$ 20°. Crystal system: orthorhombic, space group Pbc$a$, $a$ = 13.114(2), $b$ = 14.763(3), $c$ = 20.267(4) Å, $V$ = 3923.7 Å$^3$, $Z$ = 8, $D_{calc}$ = 1.294 g cm$^{-3}$, $\mu$ = 0.95 mm$^{-1}$, $T$ = 298(1) K. A total of 5054 intensities were collected in the range $\omega$ < 15° centered on the diffractometer.

Results and Discussion

Azobenzene smoothly replaces a trimethylphosphine ligand in CoCp(PMe$_3$)$_2$ according to eq. (3).

$$\text{Co(C,H)$_3$(PMe$_3$)$_2$} + \text{Ph}=\text{N}=\text{N}=\text{Ph} \rightarrow \text{Co(C,H)$_3$(PhNNPh)(PMe$_3$)} + \text{PMe$_3$}$$

From pentane in the cold dark blue crystals of 1 are obtained in 71% yield that are stable in air for 3 min and under nitrogen melt at 114–115 °C without decomposition. Solutions in ether or toluene are rapidly oxidized if air is admitted. Under argon NMR spectra show the expected signals for Cp, PMe$_3$ and azobenzene groups with correct intensities and multiplicities consistent with free rotation of all ligands. The lack of $^{31}$P coupling to C$_6$H$_5$ protons and an averaged PCH$_3$ doublet in the presence of free ligand shows rapid dissocia-

* Further details of the structure determinations have been deposited as Supplementary Material CSD 320549 (1) and CSD 320548 (6). Copies can be obtained through the Fachinformationszentrum Karlsruhe GmbH, D-W-7514 Eggenstein-Leopoldshafen, by citing the depository number, the names of the authors and the full literature citation.
tion of phosphine at 20 °C, although from refluxing toluene I is recovered unchanged. Extrusion of C2H6 by an ortho-metallation reaction as in eq. (4) has not been observed.

With CoMe(PMe3)4 a reaction according to eq. (4) rapidly proceeds at -60 °C.

\[
\text{CoCH}_3(P\text{Me}_3)_4 + \text{Ph-N=N-C}_6\text{H}_4\text{R} \rightarrow \begin{cases} \text{Co}(2-\text{C}_6\text{H}_5\text{N}=\text{N}-\text{C}_6\text{H}_4\text{R})(\text{PMe}_3)_3 + \text{CH}_4 + \text{PMe}_3 & A \\ \text{Co}(2-\text{C}_6\text{H}_5\text{N}=\text{N}-\text{C}_6\text{H}_4\text{R})(\text{PMe}_3)_3 + \text{CH}_4 & B \end{cases}
\]

(4)

<table>
<thead>
<tr>
<th>R</th>
<th>H</th>
<th>OAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(2A = 2B)</td>
<td>3A + 3B (1:1)</td>
<td></td>
</tr>
</tbody>
</table>

After π-coordination of trans-azobenzene either phenyl group can undergo ortho-metallation. Introduction of a 4-acetoxo substituent reveals still equal chances for attack at all α-positions. No evidence for electronic steering of the metallation reaction was obtained, and a 1:1 mixture of isomers 3A and 3B was observed by NMR. From ether at -25 °C 2 forms dark red prisms that are almost insoluble in pentane but freely soluble in toluene. At 25 °C the 31P NMR spectra display a virtual triplet for three equivalent trimethylphosphines indicating strong PP coupling and fast pseudorotation of ligands as often observed in penta-coordinate complex molecules [4]. At -80 °C in the slow motion limit the 31P resonances are split into a triplet and a doublet for axial and equatorial phosphines, respectively.

The equatorial phosphine is selectively replaced by a carbonyl ligand in a slow reaction according to eq. (5) which gives virtually quantitative yield.

\[
2\text{CoCH}_3(P\text{Me}_3)_4 + \text{C}_6\text{H}_5\text{N} = \text{N} \rightarrow \text{Co}(\text{C}_6\text{H}_5\text{N} = \text{N})(\text{PMe}_3)_3 + 3\text{PMe}_3 + \text{CO}
\]

(5)

Deep red crystals of 4 when dissolved in ether or toluene show a deep violet color. A strong infrared absorption at 1918 cm⁻¹ together with a medium intensity band at 482 cm⁻¹ (and no bands around 1600 cm⁻¹ where products of a CO insertion reaction are expected to absorb) indicate only terminal CO ligands.

The cis-fixed diazene benzo[c]cinnoline cannot form a five-membered chelate ring as in 2, and therefore simply replaces a phosphine ligand in CoMe(PMe3)4 according to eq. (6).

\[
\text{CoMe(PMe}_3)_4 \rightarrow \text{CoMe(C}_6\text{H}_5\text{N}_2)(\text{PMe}_3)_3 + \text{PMMe}_3
\]

(6)

CoR(PMe3)4 (R = C6H5, C=CC6H5) do not react under these conditions. From THF/pentane 5 forms violet plates that are sensitive to air and moisture and under argon decompose above 80 °C. The presence of the CoCH3 group is recognized by an infrared band at 1158 cm⁻¹ (δCoCH3) and by a triplet proton resonance at -0.25 ppm. Coupling of an axial CoCH3 group with two equatorial 31P nuclei (3J(31P) = 0.9 Hz) and no resolved coupling (3J(31P) < 0.5 Hz) with the axial 31P nucleus as in CoMe(PMe3)4 [4] leaves an equatorial position for π-coordinated benzo[c]cinnoline. Separate PCH3 resonances for axial and equatorial phosphines are observed accordingly.

Combining CoCp(PMe3)2 and benzo[c]cinnoline establishes an equilibrium (7) which is shifted to either side by adding the appropriate neutral ligand.

\[
2\text{CoCp(PMe}_3)_2 + \text{C}_6\text{H}_5\text{N}_2 \rightleftharpoons \text{CoCp}_2(\text{C}_6\text{H}_5\text{N}_2)(\text{PMe}_3)_2 + 3\text{PMe}_3
\]

(7)

In THF solution a third species is present which is elusive and makes fractional crystallization difficult and considerably reduces yields of pure 6. The dark green shining crystals of 6 are air-sensitive and under argon decompose above 135 °C. NMR spectra obtained from toluene solutions present a doublet proton resonance for coordinated phosphine (9H), a singlet for Cp (10H), and multiplets for benzo[c]cinnoline (8H). At -100 °C broadening of the Cp resonance occurs (Δν1/2 = 140 Hz) while the other signals and the PCH3 doublet in particular remain sharp (Fig. 1). At still lower temperatures two discrete Cp signals are expected to arise from the presence and absence of trimethylphosphine at the two equivalent cobalt sites in the slow-motion limit. Clearly the composition of 6 requires lone-pair coordination of the diazene functions. It was therefore of prime interest to compare the structural features of 1 and 6 by means of an X-ray structure investigation.
Both crystals contain isolated molecular units. Fig. 2 and 3 give the atom numbering and principal bond distances and angles. The cobalt atom in 1 is surrounded by an $\eta^5$-C$_5$H$_5$ group, a phosphine at a distance Co–P = 2.188(2) Å which is typical for cobalt(I) [6] and a trans-azobenzene ligand $\eta^5$-coordinated at slightly different distances Co–N = 1.913(6) and 1.965(5) Å. The N=N distance (N1–N2 = 1.367(9) Å) is increased by 10% as compared with azobenzene (N=N = 1.243 [7]), and the phenyl groups are bent away from the metal. According to a suggestion made by Ibers [8] coordination of an azobenzene is characterized by a dihedral angle $\varphi$ between the planes N1–N2–C$_{ipso}$ and N1–N2–C$_{ipso}'$ (Fig. 2), where $\varphi = 0$ in free azobenzene. In 1 this angle ($\varphi = 11^\circ$) falls outside the generally observed range 25.5$^\circ$ $\leq$ $\varphi$ $\leq$ 43$^\circ$ [8, 9], indicating a particular weak $\pi$-co-
ordination. Consequently, azobenzene is not coordinated by less electron-rich cobalt(I) complexes \( \text{CoX(PE}_{3})_3 \) (\( X = \text{Cl} \) [9], \( \text{C}_6\text{F}_5 \) [10]) offering only a 16-electron count. However, coordination of nitrogen lone-pairs becomes a favorable alternative. In the structure of the dinuclear complex 6 this is realized exclusively, because both cobalt atoms lie in the molecular plane \((xz)\) of benzo[c]cinnoline (Fig. 3) excluding side-on CoNN' interaction. End-on bonds Co-N = 1.905(3) and 1.850(2) Å in 6 are shorter than in \( \pi \)-coordinated 1 in line with expectation. An increase of 7.8 pm in N-N bonding (1.370(4) against 1.292 Å in benzo[c]cinnoline [12]) is indicative of \( \pi \)-acceptor interactions involving antibonding NN' and a \( d_{yz} \) orbital at each metal.

![Fig. 3. Molecular structure of 6 (ORTEP plot without hydrogen atoms). Important bond distances (Å) and angles (°): Co1–Co2 2.491(1), Co1–P1 2.156(1), Co1–N1 1.905(3), Co1–C 2.061(5)–2.139(5), Co1–Cp30 1.716, Co2–N2 1.850(2), Co2–C 2.100(3)–2.129(4), Co2–Cp20 1.734, N1–N2 1.370(4), N1–C12 1.367(4), N2–C1 1.403(4), C1–C6 1.408(4), C6–C7 1.450(5), C7–C12 1.417(5), Co2–Co1–P1 87.5(1), Co2–Co1–N1 72.2(1), P1–Co1–N1 92.1(1), Co1–Co2–N2 73.0(1), Co1–N1–N2 105.9(2), Co1–N1–C12 131.9(2), N2–N1–C12 122.2(3), Co2–N2–N1 108.8(2), Co2–N2–C1 132.9(2), N1–N2–C1 118.2(2), N2–C1–C6 122.3(3), C1–C6–C7 118.2(3), C6–C7–C12 117.1(3), N1–C12–C7 121.9(3), Co2–Co1–Cp30 127.7, P1–Co1–Cp30 129.5, N1–Co1–Cp30 132.9, Co1–Co2–Cp20 137.9, N2–Co2–Cp20 148.8. (Cp = center of C5H5 ring).]
Both cobalt atoms bear \( \eta^2-C_5H_5 \) groups on one side of the diazene plane while on the opposite side and almost perpendicular to the diazene plane (N1–Co1–P1 = 92.1(1)°) a trimethylphosphine resides at Co1. An equivalent site at Co2 remains vacant but there is some angular relaxation of Cp20 towards the empty position as expressed by the differences of angles N2–Co2–Cp20–N1–Co1–Cp30 = 15.9° and Co1–Co2–Cp20–Co2–Co1–Cp30 = 15.2°. The trimethylphosphine does not accept a bridging position above the metal to metal bond (6: Co–Co = 2.491(1) Å, cobalt metal: 2.206 Å [13]) and appears to be only slightly leaning towards Co2 (Co2–Co1–P1 = 87.5(1)°). However, one can easily imagine the phosphine moving over a bridging transition state to Co2 and the molecule 6 relaxing to an identical ground-state as indicated by dynamic NMR spectroscopy.

Financial support of this work by Fonds der Chemischen Industrie and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

     b) M. I. Bruce, Angew. Chem. 89, 73 (1977); Angew. Chem., Int. Ed. Engl. 16, 73 (1977);
     c) G. W. Parshall, Acc. Chem. Res. 3, 139 (1977);
     e) M. Kilner, Adv. Organomet. Chem. 10, 132 (1972);
     b) N. Habadie, M. Dartiguenave, and Y. Dartiguenave, Organometallics 8, 2567 (1989).
[8] a) R. S. Dickson and J. A. Ibers, J. Am. Chem. Soc. 94, 2988 (1972);