Tuning the Steric and Electronic Properties of Chiral Rhenium Thiolate Complexes [1]

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Z. Naturforsch. 53 b, 893–899 (1998); received May 5, 1998

Rhenium Complexes, Thiolate Ligands, Structure

Reaction of the complex [CpRe(NO)(CO)2]BF4 with triisopropylphosphine gives the chiral CO substitution product [CpRe(NO)](P(i-Pr)3)(CO)BF4. The corresponding triphenylphosphine complex [CpRe(NO)(P(OPh)3)(CO)]BF4 may be obtained by oxidative CO removal. Reduction of the remaining CO ligand with NaBH4 furnishes the corresponding methyl complexes [CpRe(NO)(L)(CH3)]. The structure of [CpRe(NO)(P(i-Pr)3)(CH3)] was determined: triclinic space group P1 (No. 2), a = 8.442(4), b = 9.582(5), c = 11.820(8) Å, α = 81.81(4), β = 87.18(4), γ = 63.87(5)°, Z = 2. Reaction of the methyl complexes with HBF4 in the presence of thiols gives, after chromatographic workup, the thiolate derivatives [CpRe(NO)(L)(SR)].

Introduction

Transition metal organic chemistry owes a good part of its success to the fact that the properties of a complex can be fine-tuned by changing the steric and electronic demands of the supporting ligands. Various measures of the sizes of ligands have been advanced based on fairly crude [2] to quite sophisticated [3, 4] models. Electronic properties are usually discussed within the framework of the E/C concept [7–9]. While the interpretation of the origins of bonding effects may be debatable [5–9], it is nevertheless clear that even simple models of steric and electronic properties of ligands [2] provide useful guidelines for synthetic work.

We have recently described cationic thioaldehyde complexes [CpRu(PR'3)2(S=CHR)]* where the coordination mode of the thioaldehyde [η2(S) or η2(π,C=S)] depends on the steric and electronic properties of the phosphine ligands [10]. In the analogous rhenium complexes [CpRe(NO)(PPh3)(S=CHR)]* the side-on coordination mode prevails although η1 isomers have been implied as intermediates of the diastereoisomer equilibration [11]. Since the two different coordination modes are expected to lead to vastly different reactivities, e.g., in nucleophilic additions or cycloadditions [10], we decided to look at the influence of a change of the phosphorus ligand in these rhenium complexes. In this contribution, we describe the synthesis of the precursor thiolate complexes [CpRe(NO)(L)(SR)] (L = CO, P(OPh)3, P(i-Pr)3; R = Me, Et, CH2Ph, CH2(4-C6H4Cl), CH2(4-C6H4OMe), CH3, C2H5).

Synthesis of the Methyl Complexes [CpRe(NO)(L)(CH3)]

[CpRe(NO)(CO)2]BF4 (1), the common starting material for the required methyl complexes, is readily accessible in two steps from [Re2(CO)10] [12–14]. Heating 1 with an excess of P(i-Pr)3 in 2-butanone produces the CO substitution product 2 in acceptable yield (eq. (1)).

The triphenylphosphite complex 3 is obtained via oxidative CO removal (eq. (2)), in close analogy to the corresponding triphenylphosphine derivative [14]. 2 and 3 are yellow crystalline solids which are readily soluble in polar organic media.

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Their infrared spectra exhibit the typical decrease of \( \nu(\text{CO}) \) and \( \nu(\text{NO}) \) [P(OPh)\(_3\) > PPh\(_3\) \( \approx \) P(i-Pr)\(_3\)] with increasing donicity of the PR\(_3\) ligand. The \( ^1H \) and \( ^{13}C \) NMR spectra of 2 show the expected double sets of signals for the diastereotopic methyl groups of the P(i-Pr)\(_3\) ligand.

The hydride reduction of coordinated CO has been described previously by Casey [15], Graham [16], and Gladysz [14, 17]. The new chiral rhenium methyl complexes 4 and 5 were obtained similarly in good yields (eq. (3)) as orange (4) or yellow (5) crystalline solids which are soluble in all common organic solvents. The formation of a rhenium-coordinated methyl group is readily diagnosed from a high-field doublet in the \( ^{13}C \) NMR spectra.

Structure Determination of the Chiral Methyl Complex \([\text{CpRe(NO)}\{\text{P(i-Pr)}\}_3\}\{(\text{CH}_3)\}\) (4)

Crystals of 4 suitable for structure determination were grown from benzene/hexane. Fig. 1 shows a view of the molecule. The coordination around rhenium may be adequately described as octahedral, with the Cp ligand occupying three adjacent sites. The bond distances Re-N and Re-C (Table I) are almost equal to those of the similar complex \([\text{CpRe(NO)}\{(\text{PPh})_3\}\{(\text{CH}_2)\_\text{Ph}\}]\) [18].

The Re-P bond of 4 is slightly elongated (by 2 pm) which is an indication of the bulkiness of the P(i-Pr)\(_3\) ligand. The Re-NO group deviates slightly from linearity, possibly a result of the high electron density at the metal. Interestingly, the bond angle between the two smallest ligands, NO and CH\(_3\),
Table II. Important NMR spectroscopic data of the thiolate complexes [CpRe(NO)(L)(SR)] (7 - 9)\(^a\).

<table>
<thead>
<tr>
<th>No</th>
<th>(^1)H NMR</th>
<th>(^{13})C NMR</th>
<th>(^3)J(C,P)</th>
<th>CO</th>
<th>(^{31})P NMR</th>
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<tbody>
<tr>
<td></td>
<td>Cp</td>
<td>SCh(_2)</td>
<td>((P,C)) CO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7a(^b)</td>
<td>5.28</td>
<td>3.64</td>
<td>3.79</td>
<td>12.4</td>
<td>89.4</td>
</tr>
<tr>
<td>7c(^c)</td>
<td>5.00</td>
<td>2.57</td>
<td>3.83</td>
<td>12.7</td>
<td>91.9(^e)</td>
</tr>
<tr>
<td>8a(^d)</td>
<td>5.05</td>
<td>2.57</td>
<td>3.87</td>
<td>13.0</td>
<td>92.0(^f)</td>
</tr>
<tr>
<td>8d(^c)</td>
<td>5.05</td>
<td>3.57</td>
<td>3.76</td>
<td>12.4</td>
<td>91.8</td>
</tr>
<tr>
<td>8d(^d)</td>
<td>5.08</td>
<td>2.29</td>
<td>2.69</td>
<td>12.4(^f)</td>
<td>92.9(^c)</td>
</tr>
<tr>
<td>9a(^d)</td>
<td>5.93(^d)</td>
<td>3.71</td>
<td>3.91</td>
<td>12.9</td>
<td>92.9(^c)</td>
</tr>
<tr>
<td>9b(^d)</td>
<td>5.98(^d)</td>
<td>3.66</td>
<td>3.94</td>
<td>13.1</td>
<td>92.9(^c)</td>
</tr>
<tr>
<td>9c(^d)</td>
<td>5.92</td>
<td>3.67</td>
<td>3.86</td>
<td>12.9</td>
<td>94.7</td>
</tr>
<tr>
<td>9d(^c)</td>
<td>5.73</td>
<td>2.52</td>
<td>2.75</td>
<td>12.4(^f)</td>
<td>93.2</td>
</tr>
</tbody>
</table>

\(^a\) Further data see Experimental Section; \(^b\) recorded in CDCl\(_3\); \(^c\) recorded in C\(_6\)D\(_6\); \(^d\) recorded in [D\(_6\)]acetone; \(^e\) \(^{2}\)J(C,P) 2 Hz; \(^f\) \(^{3}\)J(H,H) 7.4 Hz.

is larger than both the P-Re-C and P-Re-N angles (Table I).

**Synthesis of the Thiolate Complexes [CpRe(NO)(L)(SR)]**

Treatment of the methyl complexes 4 - 6 with HBF\(_4\) in the presence of various thiols gives, after chromatography over silica, the desired thiolate complexes 7 - 9 in quite satisfactory yields as yellow (7, 8) to brownish-red (9) crystalline solids (eq. (4)).

\[ \text{L} \rightarrow \text{CpRe(NO)} \rightarrow \text{SiO} \rightarrow \text{ReS} \rightarrow \text{CH}_3 \]

\[ \text{HBF}_4 \quad \text{HSR} \quad \text{HBF}_4 \]

\[ 4 - 6 \quad 7 - 9 \]

<table>
<thead>
<tr>
<th>L/R</th>
<th>CH(_2)Ph</th>
<th>CH(_2)C(_6)H(_4)Cl</th>
<th>CH(_2)C(_6)H(_4)OMe</th>
<th>Et</th>
<th>Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i-Pr(_3))P</td>
<td>7a (73%)</td>
<td>8a (90%)</td>
<td>8b (91%)</td>
<td>8c (59%)</td>
<td>8d (86%)</td>
</tr>
<tr>
<td>(PhO(_3))P CO</td>
<td>9a (47%)</td>
<td>9b (51%)</td>
<td>9c (41%)</td>
<td>9d (45%)</td>
<td></td>
</tr>
</tbody>
</table>

Notable features of their NMR spectra (Table II) are the widely separated signals of the diastereotopic methylene protons of the SCh\(_2\) group and a fairly large \(^3\)J(C,P) coupling which is typical for this class of compounds [11]. The NO stretching frequency decreases markedly along the series L = CO > P(Ph\(_3\)) > P(i-Pr\(_3\)) which is an indication of increasing electron density at the metal. A comparison of analogous thiolate and methyl complexes shows that the donor strength of the thiol group almost equals that of an alkyl ligand (viz. 4 and 7a or 5 and 8a).

**Structure Determination of the Chiral Thiolate Complex [CpRe(NO){P(i-Pr\(_3\))}(SCH\(_3\))} (7e)**

A crystal of 7e was grown from an acetonitrile solution. Fig. 2 shows a view of the molecule. The structure of 7e is very similar to that of the methyl complex 4: The Re-N and N-O distances are equal within two standard deviations, while the Re-P distance is slightly larger in 7e (Table I).

![Fig. 2. Structure of [CpRe(NO){P(i-Pr\(_3\))}(SCH\(_3\))]} (7e).](image)
S-C(1) (154.6(8)°) indicates a transoid arrangement of the Re-P and S-C bonds similar to what has been found in other [CpRe(NO)(PR₃)(SR)] complexes [19].

Discussion

The dicarbonyl rhenium complex 1 undergoes CO exchange only very reluctantly. Nevertheless, trisopropylphosphine is nucleophilic enough to react with 1 under forcing conditions. For less nucleophilic phosphines and phosphites, oxidative CO removal in acetonitrile solution followed by ligand exchange [14] is a more efficient route to the desired chiral halfsandwich-type complexes [CpRe(NO)(L)(CO)]⁺. The reduction of the remaining CO ligand to a methyl group via formyl and hydroxymethylene intermediates is a peculiar reaction which is especially effective in rhenium chemistry [15 - 17, 20]. Treatment of the methyl rhenium complexes 4 - 6 with strong acid gives, via protonation at the metal and reductive elimination of methane [21], the solvent-stabilized Lewis acids [CpRe(NO)(L)]⁺. These react immediately with the added thiol, the complexes [CpRe(NO)(L)(HSR)]BF₄ thus formed are readily detectable in solution [11] but we have not made any effort to isolate them. The desired next step, the elimination of HBF₄, is induced by chromatography over silica.

The molecular structures of 4 and 7a have some peculiar features which deserve comment. Assuming an idealized octahedral geometry with the Cp ligand occupying three sites, the angles P-Re-N, P-Re-X, and N-Re-X (X = CH₃, SCH₃) should be 90° while the angles formed by these ligands and the center of the Cp ring should be 125.3°. The angles P-Re-N, Cp-Re-P, and Cp-Re-N roughly conform to this expectation. The CH₃ and SCH₃ ligands, however, are bent away from the NO group and towards the Cp ligand. This distortion must have an electronic origin. SCH₃ and CH₃ are both ligands of the π-donor type, the latter one by virtue of the interaction of the 2 combination of the C-H bonds with appropriate metal orbitals [22]. A telltale sign is the orientation of the SCH₃ group which hints at an avoided antibonding interaction of the lone pair at sulfur with the HOMO of the [CpRe(NO)(L)]⁺ complex. The SHOMO is strongly polarized towards the π-acceptor ligand NO (Fig. 3). The repulsion between this orbital and the π-type lone pair at sulfur can, therefore, be minimized by an opening up of the N-Re-S angle. This rather simplified picture neglects that under the low symmetry of these complexes all orbitals mix strongly. Nevertheless, it readily explains the geometrical distortions which are typical for complexes [CpRe(NO)(L)X] where X is a π-donating ligand.

Fig. 3. A: HOMO and SHOMO of the [CpRe(NO)(PR₃)]⁺ complex fragment. B: Repulsive interaction of the SHOMO and the π-type lone pair at sulfur.

Conclusions

Chiral thiolate complexes [CpRe(NO)(L)(SR)] are readily accessible for various ligands L (CO, P(OPh)₃, P(i-Pr)₃) spanning a range of steric and electronic properties. The SR group acts as a π-donor ligand. As a result, the molecular structure is dominated by avoided filled-filled interactions of the π-type lone pair at sulfur and the d electrons at rhenium.

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen using suitably purified solvents. [CpRe(NO)(CO)₂]BF₄ [14], [CpRe(NO)(CO)(CH₃)] [15, 16] trisopropylphosphine [23], and iodosobenzene [24] were obtained as described in the literature. All other reagents were used as purchased.

IR: Perkin-Elmer 283, Bruker IFS 25; NMR: Bruker AMX 400 (¹H, 400 MHz, TMS; ¹³C, 100 MHz, TMS; ³¹P, 162 MHz, H₂PO₄). Signals of aryl groups are uncharacteristic and have been omitted from the lists of spectral data. Melting or decomposition points were determined by differential scanning calorimetry (DSC).
\[\text{CpRe(NO)}\{P(i-Pr)\}_3\{CO\}]\text{BF}_4 (2)\]

A solution of 1 (0.98 g, 2.31 mmol) and triisopropylphosphine (1.10 g, 6.87 mmol) in 2-butane (20 ml) is heated for 30 min under reflux. The clear brown solution is evaporated to 3 ml and the product precipitated by adding diethyl ether. The yellow crystalline powder thus obtained may contain some triisopropylphosphine oxide as an impurity which, however, does not impede further reactions. An analytically pure sample was obtained by chromatography over a short (5 cm) silica column. The phosphine oxide is washed out with dichloromethane, followed by the product which is eluted with acetone. Yield 0.53 g (41%), yellow crystalline powder, m.p. 110 °C.

\[\text{CpRe(NO)}\{P(i-Pr)\}_3\{CO\}]\text{BF}_4 (2)

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1^3C NMR (CDCl3): 19.4 (s, CH3), 19.8 (s, CH3), 27.4 (d, 7(P,C) 27 Hz, CH).

\[\text{CpRe(NO)}\{P(OPh)}_3\{CH}_3\} (5)

\text{C}_5\text{H}_5\text{BF}_4\text{N}_0\text{PRe} (556.4)

Calcd C 32.38 H 4.71 N 2.52 %, Found C 32.54 H 4.85 N 2.39 %.

IR (CH2CI2): 2006 (CO), 1760 cm^{-1} (NO). ^1H NMR (CDCl3): 1.26 (dd, J(H,H) 7.2 Hz, J(PH) 16.0 Hz, CH3), 1.30 (dd, J(H,H) 7.1 Hz, J(PH) 15.5 Hz, CH3), 2.57 (dsept, J(H,H) 7.2 Hz, J(PH) 8.8 Hz, CH), 6.13 (s, C5H5). ^13C NMR (CDCl3): 19.6 (s, CH3), 19.9 (s, CH3), 28.8 (d, J(PC) 29 Hz, CH), 93.1 (s, C5H5). ^31P NMR (CDCl3): 36.5 (s).

\[\text{CpRe(NO)}\{P(\text{OPh})\}_3\{CO\}]\text{BF}_4 (3)

\text{Ci5H26BF4N}_0\text{PRe} (556.4)

0.53 g (41%), yellow crystalline powder, m.p. 110 °C.

The phosphine oxide is washed out with dichloromethane, followed by the product which is eluted with acetone. Yield 0.52 g (54%), yellow crystalline powder, m.p. 112 °C.

\[\text{CpRe(NO)}\{P(\text{OPh})\}_3\{CH}_3\} (5)

\text{C}_5\text{H}_5\text{BF}_4\text{N}_0\text{PRe} (606.6)

Calcd C 47.52 H 3.82 N 2.31%, Found C 47.92 H 3.95 N 2.30%.

IR (CH2CI2): 1665 cm^{-1} (NO). ^1H NMR ([D6]-acetone): 0.92 (d, J(P,H) 5.4 Hz, CH3), 4.88 (s, C5H5). ^13C NMR (CDCl3): 39.2 (d, J(PC) 11 Hz, CH3), 89.5 (d, J(PC) 3 Hz, C5H5). ^31P NMR ([D6]-acetone): 119.8 (s).

\[\text{CpRe(NO)}\{P(\text{OPh})\}_3\{CH}_3\} (5)

\text{C}_5\text{H}_5\text{BF}_4\text{N}_0\text{PRe} (556.4)

A suspension of 1 (0.58 g, 1.36 mmol) and NaBH4 (80 mg, 2.11 mmol) in THF (10 ml) is stirred for 2 h at 20 °C. Gas evolution is observed, and the mixture turns orange. After filtration over Celite, the solvent is removed under vacuum and the residue redissolved in benzene and filtered over silica. Upon partial evaporation the product is precipitated by adding hexane. Yield 0.36 g (83%), yellow crystalline powder, m.p. 116 °C.

\[\text{CpRe(NO)}\{P(\text{OPh})\}_3\{CH}_3\} (5)

A suspension of 1 (0.58 g, 1.36 mmol) and NaBH4 (80 mg, 2.11 mmol) in THF (10 ml) is stirred for 2 h at 20 °C. Gas evolution is observed, and the mixture turns orange. After filtration over Celite, the solvent is removed under vacuum and the residue redissolved in benzene and filtered over silica. The solution is again evaporated to dryness and the residue recrystallized from hexane. Yield 0.38 g (63%), orange crystals, m.p. 72 °C.

\[\text{CpRe(NO)}\{P(\text{OPh})\}_3\{CH}_3\} (5)

A suspension of 1 (0.58 g, 1.36 mmol) and NaBH4 (80 mg, 2.11 mmol) in THF (10 ml) is stirred for 2 h at 20 °C. Gas evolution is observed, and the mixture turns orange. After filtration over Celite, the solvent is removed under vacuum and the residue redissolved in benzene and filtered over silica. Upon partial evaporation the product is precipitated by adding hexane. Yield 0.36 g (83%), yellow crystalline powder, m.p. 116 °C.

\[\text{CpRe(NO)}\{P(\text{OPh})\}_3\{CH}_3\} (5)

A suspension of 3 (0.50 g, 0.71 mmol) and NaBH4 (80 mg, 2.11 mmol) in THF (10 ml) is stirred for 2 h at 20 °C. Gas evolution is observed, and the mixture turns orange. After filtration over Celite, the solvent is removed under vacuum and the residue redissolved in benzene and filtered over silica. Upon partial evaporation the product is precipitated by adding hexane. Yield 0.36 g (83%), yellow crystalline powder, m.p. 116 °C.
Table III. Details of the structure determinations of [CpRe(NO){P(i-Pr)}]([X]) (X = CH₃ (4), SCH₃ (7e)).

<table>
<thead>
<tr>
<th>Formula</th>
<th>4</th>
<th>7e</th>
</tr>
</thead>
<tbody>
<tr>
<td>F. wt.</td>
<td>C₁₅H₂₀NOPRe</td>
<td>C₁₅H₂₀NOPreS</td>
</tr>
<tr>
<td>Color</td>
<td>orange</td>
<td>deep yellow</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.2 × 0.2 × 0.3</td>
<td>0.8 × 0.8 × 0.6</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293(2)</td>
<td>172(3)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.70930</td>
<td>0.71073</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1 (No. 2)</td>
<td>P2₁ (No. 3)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.442(4)</td>
<td>7.0515(7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.582(5)</td>
<td>17.3469(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.820(8)</td>
<td>7.9727(7)</td>
</tr>
<tr>
<td>α (°)</td>
<td>81.81(4)</td>
<td>70.421(7)</td>
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<tr>
<td>β (°)</td>
<td>87.18(4)</td>
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<tr>
<td>γ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>849.7(8)</td>
<td>890.77(13)</td>
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<tr>
<td>Z</td>
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<tr>
<td>ρ (calc) (mg mm⁻³)</td>
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<td>1.822</td>
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<tr>
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</tr>
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<td>2.35 - 24.97</td>
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<td>3431</td>
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<td>2799</td>
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<tr>
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</tr>
<tr>
<td>Parameters</td>
<td>172</td>
<td>159</td>
</tr>
<tr>
<td>R²</td>
<td>0.0157</td>
<td>0.0356</td>
</tr>
<tr>
<td>wR²</td>
<td>0.0403</td>
<td>0.0882</td>
</tr>
</tbody>
</table>

7e: Yield 129 mg (66%), yellow crystalline powder, m.p. 124 °C.

C₁₅H₂₀NOPReS (488.6)
Calcd C 36.87 H 5.98 N 2.87 S 6.56%.
Found C 36.54 H 6.02 N 2.82 S 6.62%.

IR (CH₃Cl₂): 1634 cm⁻¹ (NO). ¹H NMR ([D₆]-acetone): 3.75 (s, OCH₃). ¹³C NMR ([D₆]-acetone): 55.4 (s, OCH₃).

8a: Yield 257 mg (90%), yellow crystalline powder, m.p. 119 °C.

C₂₁H₂₇NO₃PReS (714.8)
Calcd C 50.41 H 3.81 N 1.96 S 4.49%.
Found C 50.22 H 3.65 N 1.93 S 4.67%.

IR (CH₃Cl₂): 1680 cm⁻¹ (NO).

8b: Yield 273 mg (91%), yellow crystalline powder, m.p. 123 °C.

C₂₇H₂₈ClNO₃PReS (749.2)
Calcd C 48.09 H 3.50 N 1.87 S 4.28%.
Found C 47.72 H 3.56 N 1.84 S 4.72%.

IR (CH₃Cl₂): 1679 cm⁻¹ (NO).

8c: Yield 176 mg (59%), yellow crystalline powder, m.p. 121 °C.

C₁₃H₂₉NO₃PReS (744.8)
Calcd C 49.99 H 3.92 N 1.88 S 4.30%.
Found C 49.68 H 3.94 N 1.86 S 4.40%.

IR (CH₃Cl₂): 1678 cm⁻¹ (NO). ¹H NMR ([D₆]-acetone): 3.75 (s, OCH₃). ¹³C NMR ([D₆]-acetone): 55.4 (s, OCH₃).

8d: Yield 225 mg (86%), yellow crystalline powder, m.p. 134 °C.

C₂₅H₃₂NO₃PReS (652.7)
Calcd C 46.00 H 3.86 N 2.15 S 4.91%.
Found C 45.93 H 3.80 N 2.04 S 5.20%.

IR (CH₃Cl₂): 1677 cm⁻¹ (NO). ¹H NMR ([D₆]-acetone): 1.15 (t, J(H,H) 7.4 Hz, CH₃). ¹³C NMR ([D₆]-acetone): 20.3 (s, CH₃).

9a: Yield 81 mg (47%), maroon crystalline powder, m.p. 70 °C.

C₁₃H₂₉NO₃ReS (432.5)
Calcd C 36.10 H 2.80 N 3.24 S 7.41%.
Found C 36.13 H 3.14 N 3.03 S 7.55%.

IR (CH₃Cl₂): 1990 (CO), 1712 cm⁻¹ (NO).

9b: Yield 95 mg (51%), maroon crystalline powder, m.p. 106 °C.

C₁₃H₂₅ClNO₃ReS (467.0)
Calcd C 33.44 H 2.37 N 3.00 S 6.87%.
Found C 33.31 H 2.37 N 2.73 S 7.48%.

IR (CH₃Cl₂): 1991 (CO), 1715 cm⁻¹ (NO).

9c: Yield 76 mg (41%), maroon crystalline powder, m.p. 42 °C.

C₁₃H₂₅NO₃ReS (462.5)
Calcd C 36.35 H 3.05 N 3.03 S 6.93%.
Found C 36.24 H 2.99 N 2.61 S 7.13%.

IR (CH₃Cl₂): 1989 (CO), 1714 cm⁻¹ (NO). ¹H NMR ([D₆]-acetone): 3.75 (s, OCH₃). ¹³C NMR ([D₆]-acetone): 55.4 (s, OCH₃).

9d: Yield 67 mg (45%), maroon crystalline powder, m.p. 50 °C.

C₈H₁₀NO₂Re₂S (370.4)
Calcd C 25.94 H 2.72 N 3.78 S 8.66%.
Found C 25.90 H 2.63 N 3.72 S 8.66%.

IR (CH₃Cl₂): 1989 (CO), 1710 cm⁻¹ (NO). ¹H NMR ([D₆]-acetone): 1.19 (t, J(H,H) 7.3 Hz, CH₃). ¹³C NMR ([D₆]-acetone): 19.8 (s, CH₃).

X-ray structure determination of [CpRe(NO){P(i-Pr)}(CH₃)] (4)

Clear orange crystals suitable for structure determination were obtained from benzene/hexane solutions. 25 centered reflections from a crystal of the dimensions given...
in Table III gave a triclinic unit cell. Data were collected from one half of the reflection sphere in the range 2° < \( \Theta < 25° \) (Enraf-Nonius CAD 4 diffractometer, \( \text{MoK}_\alpha \) radiation, graphite monochromator, filter factor 15.4). An empirical absorption correction based on the counts of 9 reflections was applied. The structure was solved by Patterson methods (program SHELXS 86 [25] in the space group P-1 (Nr. 2). H atoms were included in idealized positions, coupled to their respective carbon atoms. Least-squares cycles using the SHELXL 93 program package [26] led to the R values given in Table III. The 5 highest maxima of the final difference Fourier map were all below 0.496 e \( \text{Å}^{-3} \). Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408631.

X-ray structure determination of

\[
\text{[CpRe(NO)}\{P(i-Pr)\}_2\{(SCH_i)\}] \quad (7e)
\]

Clear brown crystals suitable for structure determination were obtained from acetonitrile solution. 25 centered reflections from a crystal of the dimensions given in Table III gave a monoclinic unit cell. Data were collected from nearly one half of the reflection sphere in the range 2° < \( \Theta < 25° \) (Enraf-Nonius CAD 4 diffractometer, \( \text{MoK}_\alpha \) radiation, graphite monochromator, filter factor 16.4). An empirical absorption correction based on a \( \Psi \)-scan was applied (av. transmission 86.53%). The structure was solved by direct methods (program SHELXS 86 [25] in the space group P2\(_1\) (Nr. 3). H atoms were included in idealized positions, coupled to their respective carbon atoms. Least-squares cycles using the SHELXL 93 program package [26] led to the R values given in Table III. The 5 highest maxima of the final difference Fourier map were below 1.492 e \( \text{Å}^{-3} \). This quite large value originates from the use of a fairly large, twinned crystal. The twinning correction provided by the SHELXL 93 program package was applied. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408630.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 347 and the Fonds der Chemischen Industrie, Frankfurt/Main.