

# Reductive elimination reaction of rhenium complexes *trans*-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Re(CO)<sub>2</sub>(chloroaryl)Cl

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## Abstract

Thermal reaction of the chloroaryl-chloride complexes *trans*-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Re(CO)<sub>2</sub>(Ar<sup>Cl</sup>)Cl (Ar<sup>Cl</sup> = 3-ClC<sub>6</sub>H<sub>4</sub>, 3-ClC<sub>6</sub>H<sub>3</sub>(4-Me) and 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in acetonitrile did not interconvert to the *cis* isomer, instead the complex ReCl(CO)<sub>2</sub>(NCMe)<sub>3</sub> and the corresponding 5-Ar<sup>Cl</sup>-1,2,3,4,5-pentamethylcyclopentadiene were formed. Similar reductive elimination products were obtained when the starting rhenium complexes were reacted with trimethylphosphite in toluene.

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**Keywords:** Rhenium complexes; Reductive elimination; Chloroaryl-pentamethylcyclopentadiene

## 1. Introduction

Intramolecular alkyl and aryl migration from metal to a coordinated cyclopentadienyl ligand (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), have been usually proposed as intermediates in several substitution reactions involving cyclopentadienyl metal complexes [1]. For instance, the 16-electron complex ( $\eta^4$ -C<sub>5</sub>H<sub>5</sub>-R)WHCp, was suggested by Green, as one of the two possible intermediates which can be formed, in the photochemical reaction of Cp<sub>2</sub>WH<sub>2</sub> in xylene, to produce the dialkyl complex Cp<sub>2</sub>WR<sub>2</sub> (R = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-*p*) [2]. On the other hand, Nesmeyanov to explain the formation of W(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub> in the thermal reaction of CpW(CO)<sub>3</sub>Ph with excess of PPh<sub>3</sub>, suggested the complex ( $\eta^4$ -C<sub>5</sub>H<sub>5</sub>Ph)W(CO)<sub>3</sub>PPh<sub>3</sub> as one of the feasible intermediate [3]. Also, in a thermal reaction of Cp\*Re(CO)<sub>2</sub>Cl<sub>2</sub> (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) with excess of P(OMe)<sub>3</sub>, which leads to the formation of *mer-cis*-Re(CO)<sub>2</sub>Cl(P(OMe)<sub>3</sub>)<sub>3</sub> as the major product, we proposed the elimination of 5-chloro-1,2,3,4,5-pentamethylcyclopentadiene [4]. However, in

none of the previous cases the presence of the corresponding cyclopentadiene could be identified. More recently, an unusual coupling between perfluorobenzyl and pentamethylcyclopentadienyl ring was observed by Hughes, in the thermal reaction of Cp\*Co(CO)I(CF<sub>2</sub>C<sub>6</sub>F<sub>5</sub>) in refluxing benzene. In this case, the organic product 5-perfluorobenzyl-1,2,3,4,5-pentamethylcyclopentadiene, could be isolated by column chromatography and characterized by <sup>1</sup>H and <sup>19</sup>F NMR and GC/MS [5].

In this paper, we describe the thermal reactions of the chloroaryl-chloride complexes *trans*-Cp\*Re(CO)<sub>2</sub>(Ar<sup>Cl</sup>)Cl (Ar<sup>Cl</sup> = 3-ClC<sub>6</sub>H<sub>4</sub>, 3-ClC<sub>6</sub>H<sub>3</sub>(4-Me) and 3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with NCMe and P(OMe)<sub>3</sub> to afford the unexpected complexes ReCl(CO)<sub>2</sub>(L)<sub>3</sub> (L = NCMe, P(OMe)<sub>3</sub>) and the corresponding 5-Ar<sup>Cl</sup>-1,2,3,4,5-pentamethylcyclopentadiene. The organic and organometallic products were isolated and characterized by spectroscopic techniques.

## 2. Results and discussion

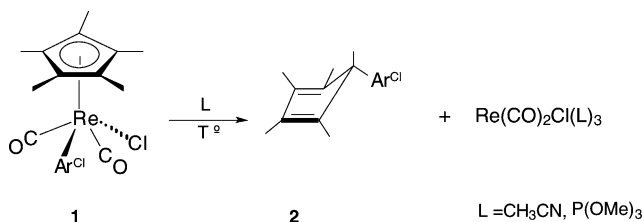
For several years we have been involved in investigating the C–Cl bond activation of chloroaromatic compounds from the photogenerated rhenium fragment Cp\*Re(CO)<sub>2</sub>

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[6–9]. We have successfully achieved the insertion of the rhenium fragment in a quite large number of chlorobenzene [6,7] and chloroarene [8,9] molecules to form complexes, possessing a “four legged piano-stool” type of structure with a general formula  $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$ . Since in most of the cases, the isolated products possess a *trans* stereochemistry and considering the current interest on the *cis*  $\leftrightarrow$  *trans* isomerization reactions of complexes of the type  $\text{CpML}_2\text{L}'_2$ , both in solution [10] and confined environments [11], we undertook a research program to study the experimental conditions which allow us to achieve *trans* to *cis* isomerization of the complexes *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$  ( $\text{Ar}^{\text{Cl}} = 3\text{-ClC}_6\text{H}_3(4\text{-Me})$  [9],  $3,5\text{-Cl}_2\text{C}_6\text{H}_3$  [7] and  $3\text{-ClC}_6\text{H}_4$ ) in acetonitrile. Unfortunately, in none of the cases was the *cis* isomer observed, instead the  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{CN}$  at room temperature showed, in the region  $\delta$  1–2, the slow disappearance of the  $\text{Cp}^*$  resonance and the emergence of three new signals. Changes were also observed in the aromatic region. The transformation occurs much faster at  $40^\circ\text{C}$  and the starting complex disappeared completely (by IR) after 4 h. The products shown in Scheme 1, were separated by column chromatography.

The cyclopentadiene derivatives isolated as white solids, were easily identified by  $^1\text{H}$  NMR and MS. The  $^1\text{H}$  NMR spectra of these compounds showed resonances for the three distinct methyl groups at about  $\delta$  1.3 (3H), 1.5 (6H) and 1.8 (6H). The up field signal was assigned to the methyl group bound to  $\text{sp}^3$  carbon atom and the two low field resonances assigned to the methyl's bounds to the olefinic carbons of the C-5 ring. This assignment is in good agreement with those reported by Hughes [5] and King [12] for 5-perfluorobenzyl-1,2,3,4,5-pentamethylcyclopentadiene and 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene, respectively. The presence of the chloroaryl substituent in these molecules was inferred from the corresponding substitution pattern of the aryl ring. The  $^{13}\text{C}$  NMR spectra are also in agreement with the proposed structure. Further confirmation of the structure of these compounds was obtained from mass spectrometry. In the three cases, the spectra showed the molecular ion  $\text{M}^+$  and the successive loss of two methyl groups.

Turning now to the organometallic products, the tris-acetonitrile complex  $\text{ReCl}(\text{CO})_2(\text{NCMe})_3$  obtained in the



$\text{Ar}^{\text{Cl}} = 3\text{-ClC}_6\text{H}_3(4\text{-Me})$  (a);  $3,5\text{-Cl}_2\text{C}_6\text{H}_3$  (b) and  $3\text{-ClC}_6\text{H}_4$  (c)

Scheme 1. Thermal reactions of *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$  with acetonitrile or trimethylphosphite.

thermolysis of *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$  in acetonitrile was isolated as white solid, which exhibits an IR spectrum with two strong  $\nu(\text{CO})$  absorptions at  $1927$  and  $1840\text{ cm}^{-1}$  in MeCN. The  $^1\text{H}$  NMR spectrum of this complex, in acetonitrile- $d_6$ , showed two resonances at  $\delta 1.95$  and  $2.46$  with an intensity ratio of 1:2 which are assigned to the protons of the two different acetonitrile ligands. Even though the  $^{13}\text{C}$  NMR spectrum exhibits a single resonance for the methyl's carbons of the acetonitrile ligands ( $\delta$  4.3), the low field region of the spectrum confirms the presence of two distinct ligands, since it shows a pair of resonances ( $\delta$  119.4 and 123.4, and  $\delta$  194.7 and 199.5) for the carbons of the CN and CO groups, respectively. Taking into account the above results, two possible isomers, *mer-cis* or *fac* can be proposed for  $\text{ReCl}(\text{CO})_2(\text{NCMe})_3$ . Unfortunately, the lack of information about mononuclear rhenium acetonitrile complexes precludes us to assign unequivocally the stereochemistry for this complex. Further work, possibly an X-ray crystallographic study, is needed to discard one of the two possible isomers.

In order to investigate if the reductive elimination of aryl-pentamethylcyclopentadiene molecules is induced by other two electron donor ligands, we carried out the thermal reaction of the three complexes *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$  with an excess of trimethylphosphite at  $40^\circ\text{C}$  in toluene (Scheme 1,  $\text{L} = \text{P}(\text{OMe})_3$ ).

In all cases, we observed the formation of the same reductive elimination products, which exhibited identical spectroscopic parameters already mentioned. The organometallic product formed in these reactions, exhibited identical spectroscopic parameters reported for the complex *mer-cis*- $\text{ReCl}(\text{CO})_2(\text{P}(\text{OMe})_3)_3$  [4] (IR and  $^1\text{H}$  NMR) and similar to those found for *mer-cis*- $\text{MnBr}(\text{CO})_2(\text{P}(\text{OEt})_3)_3$  [13].

According to the above results and considering that the starting complexes remained unchanged in toluene- $d_8$  under similar conditions ( $40^\circ\text{C}$  and 4 h), we believe that the two electron donor ligand (acetonitrile or trimethylphosphite) induces an intramolecular coupling reaction of the chloroaryl and pentamethylcyclopentadienyl ligands to give the corresponding chloroaryl-cyclopentadiene and the octahedral chlorodicarbonyl rhenium(I) complex  $\text{ReCl}(\text{CO})_2(\text{L})_3$ . By considering that the Re centre in the starting complexes *trans*- $\text{Cp}^*\text{Re}(\text{CO})_2(\text{Ar}^{\text{Cl}})\text{Cl}$ , is sterically crowded, probably the first step of the reaction should involve the migration of the aryl group to the  $\text{Cp}^*$  ligand with simultaneous reduction of Re(III) to Re(I) to give the unobserved diolefinic intermediate ( $\eta^4\text{-C}_5\text{Me}_5\text{Aryl}$ )- $\text{ReCl}(\text{CO})_2(\text{L})$ . Further reaction of the intermediate with excess of L should displace the 5-chloroaryl-1,2,3,4,5-pentamethylcyclopentadiene and form the octahedral rhenium complex.

Taking into account the results described above and those previously reported for similar complexes, containing different chloroaryl ligands [6–9] it is clear that the substituents on the aryl ligand plays an important role in deter-

mining the type of the reaction observed when complexes *trans*-Cp\*Re(CO)<sub>2</sub>(Ar<sup>Cl</sup>)Cl, are dissolved in acetonitrile. However, at this point we can not conclusively discard that steric and/or electronic effects on the aryl ligand are influencing factors affecting the preference of the starting complexes to undergo the reductive coupling reactions instead of isomerization. Studies on a more complete series of this type of complexes possessing different aryl and halide ligands are currently underway to further evaluate these issues.

### 3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Cp\*Re(CO)<sub>3</sub> was prepared according to a procedure described in the literature [14]. 1,3-Dichlorobenzene and trimethylphosphite (Aldrich) were used as received. Complexes *trans*-Cp\*Re(CO)<sub>2</sub>(3-C<sub>6</sub>H<sub>3</sub>Cl-4-Me)Cl and *trans*-Cp\*Re(CO)<sub>2</sub>(3,5-C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>)Cl were prepared as previously reported [7,9]. Photochemical reaction was carried out on a Rayonet RPR 100 photoreactor. Infrared spectra were recorded in solution (CaF<sub>2</sub> cell) on a Perkin–Elmer FT-1605 spectrophotometer, <sup>1</sup>H and <sup>13</sup>C NMR spectra on a Bruker ADVANCE 400 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances, <sup>13</sup>C chemical shifts to solvent peaks. Mass spectra were obtained at the Laboratorio de Servicios Analíticos, Universidad Católica de Valparaíso. Elemental analyses were obtained at the Centro de Instrumentación, P. Universidad Católica de Chile, Santiago, Chile.

#### 3.1. *trans*-Cp\*Re(CO)<sub>2</sub>(3-C<sub>6</sub>H<sub>4</sub>Cl)Cl (**1c**)

Five Pyrex tubes containing Cp\*Re(CO)<sub>3</sub> (100 mg; 0.247 mmol) dissolved in 15 mL of 1,3-dichlorobenzene, were irradiated at 350 nm for 15 h. The resulting light yellow solutions were mixed and the solvent was removed under vacuum. The residue was chromatographed on silica gel column. Elution with hexanes moved the unreacted Cp\*Re(CO)<sub>3</sub> (440 mg, 1.08 mmol). Hexanes/CH<sub>2</sub>Cl<sub>2</sub> (5:1) moved an orange band of *trans*-Cp\*Re(CO)<sub>2</sub>(3-C<sub>6</sub>H<sub>4</sub>Cl)Cl containing traces of Cp\*Re(CO)<sub>2</sub>Cl<sub>2</sub>. Recrystallization of this mixture afforded pure orange crystals of *trans*-Cp\*Re(CO)<sub>2</sub>(3-C<sub>6</sub>H<sub>4</sub>Cl)Cl (yield 25 mg, 0.048 mmol, 32% conversion).

IR (CH<sub>2</sub>Cl<sub>2</sub>, ν(CO)/cm<sup>-1</sup>): 2036s and 1957vs; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.72 (s, 15H), 7.05 (m, 2H), 7.49 (td, J<sub>H-H</sub> = 7.2, 1.6 Hz, 1H), 7.58 (t, J<sub>H-H</sub> = 1.6 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ: 9.3 (C<sub>5</sub>Me<sub>5</sub>), 103.5 (C<sub>5</sub>Me<sub>5</sub>); 125.3; 128.8; 129.9; 134.4; 143.4; 144.6 (C<sub>6</sub>H<sub>4</sub>Cl) (C<sub>6</sub>H<sub>4</sub>Cl), 196.9 (CO); mass spectrum (based on <sup>187</sup>Re/<sup>35</sup>Cl) *m/z* 524 [M]<sup>+</sup>, 496 [M-CO]<sup>+</sup>, 468 [M-2CO]<sup>+</sup>, 356 [M-2CO-C<sub>6</sub>H<sub>4</sub>Cl]<sup>+</sup>. Anal. Calc. for C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>Cl<sub>2</sub>Re: C, 41.22; H, 3.65. Found: C, 40.09; H, 3.82%.

#### 3.2. Thermal reactions of the complexes *trans*-(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Re(CO)<sub>2</sub>(chloroaryl)Cl (**1**) with acetonitrile

##### 3.2.1. General procedure

Acetonitrile solutions containing the complexes **1** (100 mg) were heated under N<sub>2</sub> at 40 °C for 4 h. An IR spectrum recorded after this time, showed the complete disappearance of the two absorption bands of the starting rhenium complexes and the appearance of two strong absorptions at 1927 and 1840 cm<sup>-1</sup>. The reaction mixture was concentrated under vacuum to dryness. The residue was washed with hexanes 3 × 10 mL and filtered through a short column of Celite. The insoluble material was dissolved in CH<sub>3</sub>CN and filtered through Celite. Vacuum evaporation of acetonitrile afforded a white solid of the complex ReCl(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>3</sub> (**3**) (~70% yield).

IR (CH<sub>3</sub>CN, ν(CO)/cm<sup>-1</sup>): 1927 s and 1840 s; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ: 1.95 (s, 3H, CH<sub>3</sub>CN), 2.46 (s, 6H, CH<sub>3</sub>CN). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN) δ: 4.3 (s, CH<sub>3</sub>CN); 119.4 (s, CH<sub>3</sub>CN); 123.4 (s, CH<sub>3</sub>CN); 194.7 (s, CO); 199.5 (s, CO). M.p. 180 °C with decomposition. Anal. Calc. for C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>ClRe: C, 26.74; H, 2.51. Found: C, 27.01; H, 2.40%.

The hexane solution was concentrated ca. 5 mL and chromatographed on a neutral alumina column (10 cm). Elutions with hexanes moved the corresponding complexes **2**, which were obtained as a white solid after vacuum evaporation of the solvent. A mixture hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1) moved small amount of the complex (**3**).

##### 3.2.2. 5-(3-Chloro-4-methylphenyl)-1,2,3,4,5-pentamethylcyclopentadiene (**2a**)

From 100 mg (0.186 mmol) of **1a**, 39 mg (0.150 mmol) of compound **2a** was isolated as white microcrystals. Yield: 71%. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ: 1.27 (s, 3H); 1.55 (d, J = 0.5 Hz, 6H); 1.83 (d, J = 0.5 Hz, 6H); 2.33 (s, (3-C<sub>6</sub>H<sub>3</sub>Cl(4-CH<sub>3</sub>)), 3H); 6.84 (dd, J = 7.9, 1.8 Hz, 1H); 6.93 (d, J = 1.8 Hz, 1H); 7.18 (d, J = 7.9 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ: 10.0 (s, C<sub>5</sub>Me<sub>5</sub>); 11.2 (s, C<sub>5</sub>Me<sub>5</sub>); 18.5 (s, C<sub>5</sub>Me<sub>5</sub>); 19.5 (s, 3-C<sub>6</sub>H<sub>3</sub>Cl(4-CH<sub>3</sub>)); 59.9 (s, C<sub>5</sub>Me<sub>5</sub>); 124.6; 126.8; 130.6; 133.0; 134.1; 134.2; 142.3; 143.6 (s, olefinic and aromatic carbons). Mass spectrum *m/z*: 260 [M]<sup>+</sup>, 245 [M<sup>+</sup>-Me], 230 [M<sup>+</sup>-2Me], 210 [M<sup>+</sup>-Cl-Me]. M.p. 59 °C. Anal. Calc. for C<sub>17</sub>H<sub>21</sub>Cl: C, 78.46; H, 8.08. Found: C, 78.50; H, 8.10%.

##### 3.2.3. 5-(3,5-Dichlorophenyl)-1,2,3,4,5-pentamethylcyclopentadiene (**2b**)

From 100 mg (0.179 mmol) of **1b** 36 mg (0.129 mmol), compound **2b** was isolated as white solid. Yield: 72%. <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ: 1.29 (s, 3H), 1.56 (d, J = 0.4 Hz, 6H), 1.84 (d, J = 0.4 Hz, 6H), 6.92 (d, J = 1.9 Hz, 2H), 7.27 (t, J = 1.9 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ: 9.9 (s, C<sub>5</sub>Me<sub>5</sub>); 11.2 (s, C<sub>5</sub>Me<sub>5</sub>); 18.2 (s, C<sub>5</sub>Me<sub>5</sub>), 60.1 (s, C<sub>5</sub>Me<sub>5</sub>), 124.9, 125.9, 134.6, 135.0, 143.2, 146.9 (s, olefinic and aromatic carbons). Mass spectrum *m/z*: 280 [M]<sup>+</sup>, 265 [M<sup>+</sup>-Me], 250 [M<sup>+</sup>-2Me], 230 [M<sup>+</sup>-Cl-Me]. M.p. 69 °C.

Anal. Calc. for  $C_{16}H_{18}O_2Cl_2$ : C, 68.86; H, 6.43. Found: C, 68.95; H, 6.45%.

### 3.2.4. 5-(3-Chlorophenyl)-1,2,3,4,5-pentamethylcyclopentadiene (**2c**)

From 100 mg (0.190 mmol) of **1c**, 39 mg (0.159 mmol) compound **2c** was isolated as white microcrystals. Yield: 74%.  $^1H$  NMR ( $CD_3CN$ )  $\delta$ : 1.25 (s, 3H), 1.55 (d,  $J = 0.6$  Hz, 6H), 1.84 (d,  $J = 0.6$  Hz, 6H), 6.95 (m, (3- $C_6H_4Cl$ ), 2H), 7.18 (m,  $J = 8.0$  Hz, (3- $C_6H_4Cl$ ), 2H), 7.25 (m, (3- $C_6H_4Cl$ ), 2H).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ )  $\delta$ : 10.0 (s,  $C_5Me_5$ ); 11.2 (s,  $C_5Me_5$ ); 18.4 (s,  $C_5Me_5$ ); 60.2 (s,  $C_5Me_5$ ); 124.5, 125.8, 126.3, 129.4, 133.9, 134.4, 143.6, 145.2 (s, olefinic and aromatic carbons). Mass spectrum  $m/z$ : 246 [ $M^+$ ], 231 [ $M^+ - Me$ ], 216 [ $M^+ - 2Me$ ], 196 [ $M^+ - Cl - Me$ ]. M.p. 40 °C. Anal. Calc. for  $C_{16}H_{19}O_2Cl$ : C, 78.05; H, 7.72. Found: C, 78.04; H, 7.70%.

### 3.3. Thermal reactions of the complexes *trans*-( $\eta^5$ - $C_5Me_5$ )-*Re*(CO)<sub>2</sub>(chloroaryl)Cl (**1**) with trimethylphosphite

Toluene solutions containing complexes **1** (50 mg) were reacted with an excess (0.1 mL) of  $P(OMe)_3$  at 40 °C, for 4 h. The IR spectrum recorded after this time, showed only two strong absorption bands at 1980 and 1884  $cm^{-1}$  in  $CH_2Cl_2$ . The reaction mixture was concentrated under vacuum to dryness and then extracted with  $3 \times 10$  mL of hexanes. From the hexanes solution the corresponding compound **2** were isolated as described above. The residual white solid was characterized by IR and  $^1H$  NMR spectroscopy. IR ( $CH_2Cl_2$ ,  $\nu(CO)/cm^{-1}$ ): 1980 s and 1884 s.  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 3.75 (t,  $J = 10.3$  Hz, 18H,  $P(OMe)_3$  *trans* each other); 3.77 (d,  $J = 5.4$  Hz,  $P(OMe)_3$  *trans* to CO).

Mass spectrum (based on  $^{187}Re/^{35}Cl$ )  $m/z$ : 650 [ $M^+$ ], 622 [ $M^+ - CO$ ], 594 [ $M^+ - 2CO$ ], 498 [ $M^+ - CO - P(OMe)_3$ ].

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### References

- [1] J.M. O'Connor, C.P. Casey, Chem. Rev. 87 (1987) 307.
- [2] M. Berry, K. Elmitt, M.L.H. Green, J. Chem. Soc., Dalton Trans. 1950 (1979).
- [3] A.N. Nesmeyanov, N.A. Ustynyuk, L.V. Bogatyreva, L.G. Makarova, Izv. Acad. Nauk. SSSR, Ser. Khim. 55 (1973).
- [4] A.H. Klahn, S. Arenas, Bol. Soc. Chil. Quim. 38 (1993) 277.
- [5] R.P. Hughes, D.C. Lindner, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 5678.
- [6] A.H. Klahn, A. Toro, B. Oelckers, G. Buono-Core, V. Manriquez, O. Wittke, Organometallics 19 (2000) 2580.
- [7] A.H. Klahn, M. Carreño, F. Godoy, B. Oelckers, A. Pizarro, A. Toro, A. Reyes, J. Coord. Chem. 54 (2001) 379.
- [8] A. Aballay, F. Godoy, G.E. Bouno-Core, A.H. Klahn, B. Oelckers, M.T. Garland, J.C. Muñoz, J. Organomet. Chem. 688 (2003) 168.
- [9] A. Aballay, E. Clot, O. Eisenstein, M.T. Garland, F. Godoy, A.H. Klahn, J.C. Muñoz, B. Oelckers, New J. Chem. 29 (2005) 226.
- [10] L. Cheng, N.J. Coville, Organometallics 15 (1996) 867; C.P. Casey, R.S. Tanke, P.N. Hazin, C.R. Kemnitz, R.J. McMahon, Inorg. Chem. 31 (1992) 5474.
- [11] N.J. Coville, D.C. Leventis, Eur. J. Inorg. Chem. (2002) 3067.
- [12] R.B. King, W.M. Douglas, A. Efraty, Org. Synth. CV 6 (1988) 39.
- [13] R.H. Reimann, E. Singleton, J. Chem. Soc., Dalton Trans. (1973) 841.
- [14] A.T. Patton, C.E. Strouse, C.B. Knobler, J.A. Gladysz, J. Am. Chem. Soc. 105 (1983) 5804.