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# A ketone complex by alkylation of an acyl anion. Synthesis, crystal structure and spectroscopic characterization of [Cp(CO)<sub>2</sub>Re{OC(Me)Ph}]

M. Bergamo<sup>a</sup>, T. Beringhelli<sup>a</sup>, G. D'Alfonso<sup>a,\*</sup>, D. Maggioni<sup>a</sup>, P. Mercandelli<sup>b,\*</sup>, A. Sironi<sup>b</sup>

> <sup>a</sup> Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, via Venezian 21, 20133 Milan, Italy <sup>b</sup> Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via Venezian 21, 20133 Milan, Italy

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Dedicated in honor of Professor Pierre Braunstein

#### Abstract

Reaction of Li[Cp(CO)<sub>2</sub>Re(COPh)] (1) with CF<sub>3</sub>SO<sub>3</sub>Me afforded, besides the expected carbene complex [Cp(CO)<sub>2</sub>Re= C(OMe)(Ph)] (2) and the alkyl–acyl derivative [Cp(CO)<sub>2</sub>Re(Me)(COPh)] (3), a third structural isomer [Cp(CO)<sub>2</sub>Re{OC(Me)Ph}] (4), which contains an acetophenone molecule coordinated to the metal center. The X-ray analysis showed that in solid acetophenone is bound to 'CpRe(CO)<sub>2</sub>' exclusively through an oxygen  $\sigma$ -donor interaction, while in solution an equilibrium between  $\sigma$ -bound ( $\eta^1$ ) and  $\pi$ -bound ( $\eta^2$ ) forms occurs, as judged by IR data and <sup>1</sup>H and <sup>13</sup>C variable temperature NMR spectra ( $\pi/\sigma$ ratio 2.87 at 183 K and 1.16 at 263 K in CD<sub>2</sub>Cl<sub>2</sub>,  $\Delta H^\circ = -4.5$  kJ mol<sup>-1</sup> for the  $\sigma \Leftrightarrow \pi$  reaction,  $E_a$  58(1) kJ mol<sup>-1</sup>). In solvents different from Et<sub>2</sub>O (*n*-hexane, THF, acetone) and with alkylating agent different from CF<sub>3</sub>SO<sub>3</sub>Me (MeI, Me<sub>3</sub>OBF<sub>4</sub>) the formation of 4 was negligible. It has been demonstrated that 4 does not originate by acetophenone reductive elimination from 3. No evidence of the involvement of radicals has been obtained.

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# 1. Introduction

We report here on the unexpected formation of a ketone complex in the reaction of an alkylating agent with an acylrhenate salt. We met with this reaction in the course of our work aimed at preparing novel Pt–Re mixed-metal complexes. We are particularly interested in complexes that do not contain  $\pi$ -donor ligands, since these should be better suitable for catalytic trials, and in the past we prepared several of these species [1]. The last member of this series, namely the dinuclear complex

 $[Cp(CO)_2Re{\mu-CPh(OMe)}Pt(COD)]$  (COD = 1,5-cyclooctadiene) [1g], was obtained by addition of a nucleophilic Pt(COD) fragment over the Re=C double bond of the Fischer's carbene  $[Cp(CO)_2Re=C(OMe)-(Ph)]$  [2], according to the approach developed by the Stone group [3].

The original synthesis [2] of  $[Cp(CO)_2Re=C(OMe)(Ph)]$  involved protonation of the acylmetalate intermediate, followed by treatment with  $CH_2N_2$ , as shown in Eqs. (1)–(3):

$$[CpRe(CO)_3] + LiR \rightarrow Li + [Cp(CO)_2ReC(O)R]^-$$
(1)  
$$[Cp(CO)_2ReC(O)R]^-Li^+ + H^+$$

$$\rightarrow [Cp(CO)_2 ReC(OH)R] + Li^+$$
(2)

$$Cp(CO)_2ReC(OH)R] + CH_2N_2$$

$$\rightarrow [Cp(CO)_2Re=C(OMe)R] + N_2$$
(3)

To prepare [Cp(CO)<sub>2</sub>Re=C(OMe)(Ph)] we replaced

<sup>\*</sup> Corresponding authors. Tel.: +39-02-503 14351; fax: +39-02-503 14405 (G.D.A.); tel.: +39-02-503 14447; fax: +39-02-503 14454 (P.M.).

*E-mail addresses:* giuseppe.dalfonso@unimi.it (G. D'Alfonso), pierluigi.mercandelli@unimi.it (P. Mercandelli).

the above reported three-step procedure by the more direct pathway nowadays used for the synthesis of this type of carbenes, that consists in the direct alkylation of a salt of the acylmetalate anion [4]. We, therefore, treated Li[Cp(CO)<sub>2</sub>ReC(O)Ph] (Li<sup>+</sup>1, formed according to reaction 1) with the powerful methylating agent CF3SO3Me, in diethyl ether solution. A thorough study [5] of the alkylation of an acylrhenate closely related to 1, namely [Cp(CO)<sub>2</sub>ReC(O)Me]<sup>-</sup>, has previously demonstrated that alkylation can occur either at the oxygen atom of the acylate group or at the metal center, leading to a carbene or to an alkyl-acyl derivative, respectively. The site of alkylation has been shown to depend on the hardness of the alkylating agent and on the solvent, harder electrophiles and less polar aprotic solvents favoring the formation of the carbene derivatives. Neither our alkylating agent (methyl triflate) nor our solvent (diethyl ether, Et<sub>2</sub>O) was used in Bergman's study, that rather used  $R_3OPF_6$ , RI, MeOSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me (R = Me or Et) in acetone, THF or water. Under our conditions we have observed the formation not only of the products of the two above described pathways, i.e. the carbene  $[Cp(CO)_2Re=\{C(OMe)Ph\}]$  (2) and the methyl-benzoyl derivative  $[Cp(CO)_2Re(Me)\{C(O)Ph\}]$ (3), but also of a third isomer, that contains a coordinated acetophenone molecule and that does not originates from 3 (Scheme 1). The ketone molecule is  $\sigma$ bound in the solid state, while in solution an equilibrium between the  $\sigma$  and  $\pi$  forms of the ketone complex occurs, whose thermodynamics and kinetics has been investigated. To the best of our knowledge, this represents the first report of a ketone complex obtained through a similar route.

### 2. Results and discussion

The reaction of Li[Cp(CO)<sub>2</sub>ReC(O)Ph] (Li<sup>+</sup>1) with a stoichiometric amount of CF<sub>3</sub>SO<sub>3</sub>Me, at room temperature, in diethyl ether, went to completeness in approximately 2 h, affording a deep red solution, from which three main compounds were separated by chromatography on silica gel. On using a 3:1 *n*-hexane–diethyl ether mixture, three bands (yellow, red, and light-brown, respectively) were successively eluted (see Fig. 1). The first product was identified as the expected yellow



Fig. 1. IR spectra (carbonyl region, diethyl ether) of a typical mixture from the reaction of  $Li^+1$  with  $CF_3SO_3Me$  (top trace) and of the three main compounds isolated by chromatography from this mixture.

phenylmethoxy carbene **2**, even if its spectroscopic data are somewhat different from those reported in the original paper: <sup>1</sup>H NMR, C<sub>6</sub>D<sub>6</sub>,  $\delta$  4.65 (Cp), 4.16 (Me) ppm (lit. 4.92, 4.19 in the same solvent); IR v(CO) (nujol mull): 1960sh, 1940vs, 1888sh, 1872vs cm<sup>-1</sup> (lit. 1976ss, 1892ss cm<sup>-1</sup>). Samples of compound **2** synthesized in this way were successfully used for the synthesis of [Cp(CO)<sub>2</sub>Re{ $\mu$ -CPh(OMe)<sub>2</sub>}Pt(COD)] [1g], and, therefore, its formulation should be considered correct.

The third eluted product was identified spectroscopically (see Table 1) as the complex  $[Cp(CO)_2R$  $e(Me)\{C(O)Ph\}]$  (3), arising from alkylation on the rhenium atom. Particularly diagnostic for this formulation are the high filed resonance of the methyl group ( $\delta$ 0.85 ppm in C<sub>6</sub>D<sub>6</sub>) and the IR data [ $\nu$ (CO) in C<sub>6</sub>H<sub>6</sub>: 2007m, 1933s, 1603w cm<sup>-1</sup>], strictly comparable with those of the analogous methyl derivative  $[Cp(CO)_2R$  $e(Me)\{C(O)Me\}]$ , whose X-ray analysis showed a fourlegged piano stool structure with a *trans* arrangement of the acyl and alkyl ligands (2004m, 1932s, 1630m cm<sup>-1</sup>, in C<sub>6</sub>D<sub>6</sub>) [5].

The red product 4 eluted between 2 and 3 has NMR (see Table 1), mass spectra data (FAB, molecular peaks 428–426) and elemental analysis that suggest its formulation as an isomer of the two above species. This was confirmed by a single crystal X-ray analysis, that revealed the presence of an acetophenone molecule,  $\sigma$ -coordinated through the oxygen atom (Fig. 2).

Table 1 IR and <sup>1</sup>H NMR data for the compounds described in this work (298 K)

| Compound | ν <sub>CO</sub>                     | <sup>1</sup> H NMR        |                      |       |  |
|----------|-------------------------------------|---------------------------|----------------------|-------|--|
|          |                                     | Ph                        | Ср                   | Me    |  |
| 1        | 1918s, 1801s <sup>a</sup>           | 7.19–7.70m <sup>g</sup>   | 4.92s                | -     |  |
| 2        | 1958s, 1885s <sup>a</sup>           | 7.30-6.88 <sup>d</sup>    | 4.65s                | 4.17s |  |
|          | 1964s <sup>b</sup> , 1893s          | $7.32 - 6.99^{\text{ f}}$ | 5.31s                | 4.29s |  |
| 3        | 2010m, 1940vs, 1608 vw <sup>a</sup> | 8.00-7.88m <sup>d</sup>   | 4.53s                | 0.85s |  |
|          | 2014m, 1946vs, 1614 vw <sup>b</sup> | 7.74–7.58m <sup>e</sup>   | 5.62s                | 1.18s |  |
| 4        | 979m, 1909s, 1851w <sup>a</sup>     | 7.35-6.95m <sup>d</sup>   | 4.60s                | 2.33s |  |
|          | 1985m, 1916s, 1861w <sup>b</sup>    | 7.47-7.33m <sup>e</sup>   | 5.26s                | 2.49s |  |
| 5        | 2042s, 1959s <sup>c</sup>           |                           | 5.85s <sup>e,h</sup> |       |  |

<sup>a</sup> Diethyl ether.

<sup>b</sup> *n*-Hexane.

<sup>c</sup>  $CH_2Cl_2$ .

<sup>d</sup> Benzene-d<sub>6</sub>.

<sup>e</sup> CD<sub>2</sub>Cl<sub>2</sub>.

f Acetone-d<sub>6</sub>.

<sup>g</sup> THF-d<sub>8</sub>.

<sup>h</sup> The protons of the CH<sub>2</sub>Cl group give an AB system at  $\delta$  4.72 and 4.49, with  ${}^{2}J_{H-H} = 9$  Hz.

# 2.1. Solid state molecular structure of (acetophenone- $\kappa O$ )dicarbonyl( $\eta^5$ -cyclopentadienyl)rhenium (4)

The crystals of **4** contain neutral molecules held together by normal van der Waals interactions. Fig. 2 depicts the molecular architecture of **4** with a labelling scheme. A selection of relevant geometrical bond parameters is reported in Table 2.

The molecule, of idealized  $C_s$  symmetry, consists of a rhenium atom *pseudo*-tetrahedrally coordinated by two carbonyls, a cyclopentadienyl and a  $\sigma$ -acetophenone ligand. Unsymmetrical ketone complexes can exist as either *E* or *Z* C=O geometric isomers. Due to the very

Table 2 Selected bond lengths (Å) and angles (°) for compound 4  $^{a}$ 

| Bond lengths                                  |            |
|---|------------|
| Re(1)-C(1)                                    | 1.877(6)   |
| Re(1)-C(2)                                    | 1.866(6)   |
| $\operatorname{Re}(1) - \operatorname{cp}(1)$ | 1.938(4)   |
| Re(1)-O(3)                                    | 2.100(4)   |
| C(1)–O(1)                                     | 1.153(7)   |
| C(2)–O(2)                                     | 1.176(8)   |
| O(3)-C(8)                                     | 1.239(7)   |
| Bond angles                                   |            |
| C(1)-Re(1)-C(2)                               | 88.8(3)    |
| C(1)-Re(1)-cp(1)                              | 123.3(3)   |
| C(1)-Re(1)-O(3)                               | 97.6(2)    |
| C(2)-Re(1)-cp(1)                              | 124.2(2)   |
| C(2)-Re(1)-O(3)                               | 99.1(2)    |
| cp(1)-Re(1)-O(3)                              | 117.27(16) |
| Re(1)-C(1)-O(1)                               | 173.3(7)   |
| Re(1)-C(2)-O(2)                               | 172.4(6)   |
| Re(1) - O(3) - C(8)                           | 139.0(4)   |
| O(3)-C(8)-C(9)                                | 119.6(6)   |
| O(3)-C(8)-C(10)                               | 117.6(5)   |
| C(9)-C(8)-C(10)                               | 122.8(6)   |

<sup>a</sup> cp(1) Refers to the centroid of the cyclopentadienyl ligand.

different steric demand of the methyl and phenyl groups, the E isomer is the one observed.

As expected, the C(8)=O(3) bond length (1.239(7) Å) is slightly longer than that of free acetophenone (1.216(2) Å) [6], as a consequence of the  $\sigma$  bonding and  $\pi$  back-bonding interactions with the metal center, but substantially identical to that observed in the related [CpRe(NO)(PPh<sub>3</sub>)(MeC(O)Ph)]<sup>+</sup> complex (1.245(8) Å) [7]. The Re(1)-O(3)-C(8) bond angle, 139.0(4)° are somewhat greater than it would be expected for a bonding model involving an *sp*<sup>2</sup>-hybridized oxygen atom. However, this feature is found in nearly all  $\sigma$ -ketone complexes of transition metals, and has been



Fig. 2. ORTEP drawing of molecule 4 with labeling scheme. Hydrogen atoms were given arbitrary radii. Thermal displacement parameter ellipsoids were drawn at the 30% probability level.

attributed to additional donation from an occupied oxygen orbital to a low-lying empty metal orbital [8]. The phenyl ring is nearly parallel to the plane defined by the C(8), C(9), and O(3) atoms, in agreement with a high degree of conjugation in the coordinated acetophenone molecule.

### 2.2. Solution behavior of 4. The $\sigma-\pi$ equilibrium

The IR spectrum of solid 4 (nujol mull) shows two main v(CO) absorptions (1905s, 1890sh and 1817s  $cm^{-1}$ ) and a weak band at 1557  $cm^{-1}$ , due to the ketonic carbonyltesi p.75, in agreement with the solid state structure. The IR spectrum in solution, however, is markedly different, because it shows three main bands, whose relative intensities vary on changing the solvent (see Table 3). Moreover, one band is at wavenumbers much higher (1979 cm<sup>-1</sup> in Et<sub>2</sub>O) than those observed in solid. This indicates the presence in solution of two species (whose relative ratio varies with the solvent), that can be identified as two isomers differing for the binding mode of the ketone molecule. Indeed, it is well known [9] that aldehyde or ketone ligands can adopt either a  $\eta^1(\sigma)$  or a  $\eta^2(\pi)$  coordination of the carbonylic group, and often the solutions of their complexes contain equilibrium mixtures of the two isomers. The  $\eta^2$ -coordination involves substantial back-bonding from the metal to a vacant  $\pi^*$  orbital of the organic carbonyl [10], that is reflected in the dramatic decrease of the wavenumbers both of the v(CO) IR absorption (below 1200 cm<sup>-1</sup>) and of the <sup>13</sup>C NMR resonance (below  $\delta =$ 100 ppm) for the ketonic carbonyl [9]. Such backbonding is less important in  $\sigma$ -complexes and accordingly IR and <sup>13</sup>C NMR data for these carbonyls are much closer to the values of the free organic ligands. In the  $\pi$ -form, therefore, competition for back-bonding from the metal d-orbitals between the organic and the metal carbonyls causes the increase of the wavenumbers of the v(CO) modes of the metal-carbonyls, with respect to the analogous modes in the complexes where the ketone is  $\sigma$ -bound [11]. Similar arguments have been applied to the v(NO) mode in the numerous  $[CpRe(NO)(PPh_3)L]^+$  complexes (L = aldehyde or ketone) [12].

Table 3

Ratio between the absorbances of the  $v_{CO}$  IR bands of 4 at the highest and at the lowest wavenumbers (due to the  $\pi$  and  $\sigma$  form, respectively), in different solvents at room temperature

| Solvent           | $\pi/\sigma$ ratio |  |
|-------------------|--------------------|--|
| <i>n</i> -Hexane  | 3.6                |  |
| Et <sub>2</sub> O | 2.3                |  |
| THF               | 0.90               |  |
| Acetone           | 0.85               |  |

In the present case two v(CO) bands were expected for each isomer. The observation of only three bands indicates accidental overlap of two bands (one for each isomer): indeed in cyclohexane the two components of the band at intermediate wavenumbers (the most intense one, at 1909 cm<sup>-1</sup> in Et<sub>2</sub>O) are partially resolved. On the base of the above considerations, we attribute to the  $\pi$  isomer the v(CO) band at the highest wavenumbers (1979 cm<sup>-1</sup> in Et<sub>2</sub>O) and to the  $\sigma$  form the band at the lowest wavenumbers (1851  $\text{cm}^{-1}$ ). Theses attributions lead to a close agreement with data concerning related species: see for instance v(CO) 1992, 1912 cm<sup>-1</sup> (in Et<sub>2</sub>O) for  $[Cp(CO)_2Re(\eta^2-CH_2O)]$  [13] and 1921, 1850  $cm^{-1}$  for [Cp(CO)<sub>2</sub>Re(OEt<sub>2</sub>)] [14], that contains the labile ligand Et<sub>2</sub>O, ( $\sigma$ -donor through an oxygen atom), comparable with acetophenone.

The relative intensity of the lowest wavenumbers band increases on passing from *n*-hexane to Et<sub>2</sub>O to THF or acetone (see Table 3), indicating that polar solvents favor the  $\sigma$  form. An opposite trend was previously observed by Gladysz for some benzaldehyde cationic complexes [12a,12b] and was attributed to the fact that in the  $\pi$  isomers the positive charge remains more localized than in the  $\sigma$ -isomers, resulting in enhanced solvation energy. In our neutral species, it is likely that the  $\sigma$ -isomer acquires a higher polarity than the  $\pi$ -isomer due to the more classical donor-acceptor character of the ketone-metal  $\sigma$ -interaction with respect to the synergic donation/back-bonding interaction operative in the  $\pi$ -isomer.

Variable temperature IR spectra (both in *n*-hexane and in CH<sub>2</sub>Cl<sub>2</sub>) showed a slight variation of the relative intensities of the resonances at the highest ( $\pi$ ) and lowest ( $\sigma$ ) frequency, indicative of the increase of the  $\pi/\sigma$  ratio increases as the temperature decreases. This trend was previously observed in all the cases in which such type of equilibria was investigated [11,12,15].

The variable temperature <sup>1</sup>H and <sup>13</sup>C NMR data (Figs. 3 and 4) provided further insight into this equilibrium. In CD<sub>2</sub>Cl<sub>2</sub>, at 183 K, two sets of signals were observed (see Table 4), in the ratio approximately 1:2.7. The minor species at this temperature had sharp resonances both in the <sup>1</sup>H and <sup>13</sup>C spectra, and has been identified as the  $\sigma$ -isomer, on the bases of the position of the <sup>13</sup>C resonance of the carbonyl of coordinated acetophenone (211.3 ppm, in the ratio 1:2 vs. the unique signal of the two metal carbonyls, at 205.7 ppm) [16]. The corresponding resonance for the  $\pi$ -isomer was observed at 83.6 ppm: similar upfield values (range 60–90 ppm) are typical of  $\pi$ -complexes of aldheydes and ketones [9].

The unambiguous attribution of each signal (<sup>1</sup>H and <sup>13</sup>C) of the phenyl group could not be achieved for the extensive overlap of the resonances of the two isomers and the uncompleted averaging of the unequivalent phenylic resonances of two  $\pi$ -isomers. Indeed, at 183 K



Fig. 3. <sup>1</sup>H NMR variable temperature spectra of compound 4 (in  $CD_2Cl_2$ , 11 T). Traces have been plotted with different vertical scales. The upper trace refers to the same solution after 40 h at 295 K in  $CD_2Cl_2$ : \* acetophenone; • [CpRe(CO)<sub>3</sub>]. The inset shows the diastereotopic hydrogen atoms of **5** observed when decomposition occurred in CH<sub>2</sub>Cl<sub>2</sub>.

all the <sup>1</sup>H and <sup>13</sup>C resonances of the  $\pi$ -isomer were broad, indicating the occurrence of an exchange process between the two different  $\pi$  forms depicted in Scheme 2. Similar processes have been previously recognized for  $\pi$ bonded aldehydes [12b,17], and in the case of [CpRe-(NO)(PPh<sub>3</sub>)( $\eta^2$ -OC(H)Ar]<sup>+</sup> (Ar = *p*-C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>) [17] it was proved that the  $\pi$ - $\pi'$  interconversion occurred with the intermediacy of the  $\sigma$ -isomer. In the present case, on the contrary, the signals of the  $\sigma$ -isomer are sharp, and, therefore, this isomer cannot be involved in the interconversion of the two  $\pi$  forms. This also implies that the  $\pi$ - $\pi'$  interconversion is an intramolecular process, because dissociation would offer the chance of  $\pi$ - $\sigma$ interconversion and, therefore, would broaden also the signal of the  $\sigma$ -isomer.

In several related ketone complexes, the occurrence of interconversion between the Z and E isomers of the  $\sigma$  form was revealed by low temperature broadening of the

NMR resonances [7,18]. In the present case, the sharpness of the signals of the  $\sigma$  form even at the lowest temperature (183 K) could be due to a particularly fast E/Z exchange rate. Indeed, it has been previously observed [18] that in  $d^6$  Re complexes the presence of two filled degenerate orbital available for back-bonding leads to a low activation barrier and the two isomers are not distinguishable under conventional NMR conditions [7]. However, the lack of IR evidence for two isomers prompted us to assume that here only the *E* isomer has a significant concentration in solution, because steric hindrance between the carbonyls and the hydrogens of the phenyl ring destabilizes the *Z* isomer.

Increasing the temperature, the exchange between  $\sigma$ and  $\pi$ -isomers became faster, leading to a generalized broadening of the signals and eventually to averaged resonances (Figs. 3 and 4). The positions of these averaged resonances indicate that, as expected, the  $\pi/\sigma$ ratio decreases on increasing the temperature, from 2.9 to approximately 1. Particularly reliable for this estimate is the resonance of ketonic carbonyl (averaged signal at  $\delta$  142.5 ppm at 263 K), since the high  $\Delta\delta$  of the resonances of the  $\sigma$  and  $\pi$  forms ( $\Delta \delta = 127.7$  ppm, at 183 K) makes less significant the temperature dependence of their chemical shifts. A  $\Delta H^{\circ}$  value of -4.5 kJ mol<sup>-1</sup> was estimated for the  $\sigma \Leftrightarrow \pi$  reaction, on using the values of  $K = \pi/\sigma$  evaluated at 183 K (from the integrated intensities of the separated resonances of the two isomers, averaged values from different signals, K =2.87) and at 263 K (from the chemical shift of the molarfraction-weighted average resonance, K = 1.16). Values in the range  $7-14 \text{ kJ mol}^{-1}$  have been estimated for related equilibria involving aldehyedes [12b].

Fig. 5 shows the Arrhenius plot of the rate constants for the  $\pi \Leftrightarrow \sigma$  interconversion at different temperatures evaluated by band shape analysis of the methyl resonances (both in the <sup>1</sup>H and <sup>13</sup>C spectra) and of the <sup>13</sup>C signals of the Cp groups. The different evaluations are in satisfactory agreement and an activation energy of 58(1) kJ mol<sup>-1</sup> was accordingly obtained.

### 2.3. Decomposition of 4 in $CH_2Cl_2$

IR and NMR monitoring of the room temperature behavior of **4** in dichloromethane showed quite fast decomposition (complete in a few hours) to give free acetophenone, some [CpRe(CO)<sub>3</sub>] and the novel complex [Cp(CO)<sub>2</sub>Re(Cl)(CH<sub>2</sub>Cl)] (**5**), analogous to the previously known pentamethyl–cyclopentadienyl derivative [Cp\*(CO)<sub>2</sub>Re(Cl)(CH<sub>2</sub>Cl)] [19]. The latter species was obtained from oxidative addition of CH<sub>2</sub>Cl<sub>2</sub> to the unsaturated fragment Cp\*(CO)<sub>2</sub>Re, originated by THF loss from [Cp\*(CO)<sub>2</sub>Re(THF)]: most likely this is also the route responsible for the formation of **5** from the ketonic complex **4** (Eq. (4)). Interestingly, the addition



Fig. 4. Selected regions of <sup>13</sup>C NMR variable temperature spectra of 4: (left) carbonylic ( $\times$  4), (middle) aromatic and (right) aliphatic regions (CD<sub>2</sub>Cl<sub>2</sub>, 11 T). Inset: averaged signal due to the carbonyl of the coordinated acetophenone. The upper trace refers to the same solution after 40 h at 295 K in CD<sub>2</sub>Cl<sub>2</sub>: \* acetophenone; • [CpRe(CO)<sub>3</sub>].

to 4 of acetophenone (10 equiv.) did not change the reaction course, indicating that acetophenone dissociation is irreversible in  $CH_2Cl_2$ .

$$[Cp(CO)_2Re{OC(Me)Ph}] + CH_2Cl_2$$
  

$$\rightarrow [Cp(CO)_2Re(Cl)(CH_2Cl)] + Ph(Me)CO$$
(4)

Particularly diagnostic for the formulation of **5** is the AB pattern of the CH<sub>2</sub>Cl group, in the <sup>1</sup>H NMR

spectrum (obviously not detected when the decomposition of **4** occurred in  $CD_2Cl_2$ , top trace in Fig. 3). As expected, the  $\nu(CO)$  bands of **5** are shifted to higher wavenumbers (20 cm<sup>-1</sup>) with respect to those of the Cp\* derivative [19]. The simultaneous formation of [CpRe(CO)<sub>3</sub>] is attributable to some decomposition, causing evolution of CO, which is captured by the Cp(CO)<sub>2</sub>Re fragment.

Table 4 <sup>1</sup>H and <sup>13</sup>C NMR data of  $4\sigma$  and  $4\pi$  in CD<sub>2</sub>Cl<sub>2</sub> at 183 K ( $\delta$ , ppm, 11 T)

| Isomer | <sup>1</sup> H |              | <sup>13</sup> C |              |                      |                       |
|--------|----------------|--------------|-----------------|--------------|----------------------|-----------------------|
|        | Me             | Ср           | Me              | Ср           | CO <sub>ketone</sub> | CO <sub>metal</sub>   |
| σ<br>π | 2.63<br>2.22   | 5.32<br>5.09 | 27.6<br>29.1    | 84.9<br>92.4 | 211.3<br>83.6        | 205.7<br>202.6, 207.9 |



Fig. 5. Arrhenius plot of the rate constants for the  $\pi \leftrightarrow \sigma$  evaluated from the band shape analysis of the <sup>1</sup>H Me ( $\bigcirc$ ), <sup>13</sup>C Me ( $\diamondsuit$ ) and <sup>13</sup>C Cp ( $\nabla$ ) resonances, respectively.

# 2.4. Suggestions for the mechanism of the reaction affording 4

The formation of a ketone complex in the alkylation of an acylmetallate anion is unprecedented. The most reasonable route to 4 would be the process depicted in Eq. (5), involving reductive elimination of acetophenone from the benzoyl-methyl complex 3, followed by acetophenone coordination [20]. Ketone reductive elimination has been previously observed for the analogous acetyl-methyl complex studied by Bergman et al. (even if only at high temperature) [5], and a similar reaction has been suggested as the step responsible for the formation of free ketones in the alkylation of iron acylates by different RX reactants [21]. Moreover, a benzophenone complex has been prepared by thermolyzing a phenyl- $\eta^2$ -benzoyl zirconocene [22].

$$[Cp(CO)_2Re(Me)\{C(O)Ph\}]$$
  

$$\rightarrow [Cp(CO)_2Re\{OC(Me)Ph\}]$$
(5)

However, this assumption seems not to be valid. Spectroscopic pursuit of the alkylation reaction clearly shows that the formation of 4 is parallel (and not consecutive) to the formation of 3. Moreover, compound 3 is stable in diethyl ether solution at room temperature for a time much longer than that of the above reaction and anyway its decomposition does not afford any 4. Finally, we have observed that the amount of 4 in the reaction mixture does not increase with time (on the contrary, it tends to decrease, due to the instability of 4 in solution).

The formation of the ketone complex seems to be restricted to the use of  $Et_2O$  as solvent, methyltriflate as alkylating agent and **1** as substrate. Indeed changes of the solvent (on using either cyclohexane, or THF or acetone) and of the alkylating agent (MeI, Me<sub>3</sub>OBF<sub>4</sub>) dramatically reduced the amount of **4** (with the partial exception of cyclohexane, as described in Section 3). The alkylation of the acylmetallate Li[Cp(CO)<sub>2</sub>ReC(O)Me] (with methyltriflate in Et<sub>2</sub>O) gave the same products observed by Bergman [5], without any acetone complex.

The peculiarity of the reaction led us to investigate on the possible involvement of radical species (that might account also for some variability in the relative yields of the three main products in repeated preparations) [23]. However, no evidence for this has been so far obtained. We have observed that **4** is formed also in the dark, and that the use of freshly distilled or 'old' ethyl ether, as well as the addition of a radical scavenger (TEMPO) does not cause any significant change. ESR, also in the presence of a spin trap (2-methyl-2-nitroso-propane), did not give any clear evidence of radicals.

With all this evidence, the most reasonable explanation for the formation of **4** is direct methylation at the carbon atom of the acylate group, in an  $\eta^2$  canonical form in which the negative charge is localized just on the carbon atom (Scheme 3) [24]. This form should acquire some stability, with respect to the more common canonical forms having the charge localized on the oxygen or the metal atoms, from the well-known oxophilicity of rhenium. Indeed the  $\eta^2$ -coordination of acyl groups is quite common among the oxophilic earlytransition-metals [25], and several examples of this coordination are known also for transition metals of Groups 5–8 [26]. Therefore, we might speculate that only CF<sub>3</sub>SO<sub>3</sub>Me affords the ketone complex **4**, because



it is the most powerful (and, therefore, less selective) among the tested alkylating agents (the other, weaker, electrophyles select the methylation site on the bases of their affinity). The  $\eta^2$ -intermediate could be stabilized by the presence of the phenyl substituent (able to delocalize the negative charge on the carbon atom), and this could explain the lack of alkylation at the carbon atom in the case of the methyl derivative. More difficult to explain is the role of the solvent, since either more polar or less polar solvents, with respect to diethyl ether, contrast the formation of **4**. Further investigation on this and similar systems are therefore, required.

### 3. Experimental

The reactions were performed under nitrogen, using the Schlenk technique, and solvents deoxygenated and dried by standard methods. Literature methods were used for the preparation of CpRe(CO)<sub>3</sub> [27], Li[Cp(CO)<sub>2</sub>ReC(O)Ph] (Li<sup>+</sup>1) [2], and Li[Cp(CO)<sub>2</sub>Re-C(O)Me] [5]. IR spectra were obtained on a Bruker Vector 22 FT instrument using a 0.1 mm CaF<sub>2</sub> cell. Low temperature IR spectra were recording using a variable temperature cell (Specac P/N 21425). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AC200 and AMX500 spectrometers. The calibration of the temperature has been checked using the standard CD<sub>3</sub>OD-CH<sub>3</sub>OH solution. Mass spectra were recorded on a VG 7070EQ instrument, in the FAB+ mode, using NBA as matrix.

3.1. Reaction of  $Li^+[Cp(CO)_2ReC(O)Ph]^-(Li^+1)$ with  $CF_3SO_3Me$  in diethyl ether

# 3.1.1. Reaction at room temperature, on a preparative scale

A 100 ml Schlenk flask was charged with Li<sup>+</sup>1 (465 mg, 1.10 mmol), a stir bar and diethyl ether (35 ml). The suspension was treated at room temperature (r.t.) with a slight excess of CF<sub>3</sub>SO<sub>3</sub>Me (150  $\mu$ l, 1.32 mmol) and the mixture was stirred for 2 h approximately. In this time the color changed from yellow to deep red. The suspension was concentrated under vacuum, and separated by chromatography on silica gel with 3:1 (v/v) *n*-hexane: diethyl ether (16 × 2.5 cm), affording three main fractions (yellow, red and light brown, respectively). A colorless fraction collected between the first and the

second fractions contained mainly CpRe(CO)<sub>3</sub>. The first fraction (yellow) contained mainly 2 (which was isolated by precipitation from *n*-hexane at 193 K, yields 30% ca.) and other species, whose separation required a second chromatographic separation (silica gel  $2.5 \times 15$  cm; eluent *n*-hexane). This second chromatography afforded, as first colorless fraction, a non-carbonyl compound, identified as  $(C_6H_5)_2$  (biphenyl) by comparison with literature data [28], as second colorless fraction the species [Cp(CO)<sub>2</sub>ReMe<sub>2</sub>], identified from its IR and NMR data [5] and as third fraction the yellow compound 2. The third fraction of the first separation (light brown) was constituted by 3 (yield ca. 10% after crystallization from diethyl ether-n-hexane at 193 K). The second (red) fraction, after evaporation to dryness, afforded a residue that was crystallized from n-hexane at 193 K, yielding 4 (10% ca.). Crystals of 4 suitable for X-ray diffraction were obtained from diethyl ether-nhexane at 243 K. Anal. Calc. for C<sub>15</sub>H<sub>13</sub>O<sub>3</sub>Re: C, 42.14; H, 3.06. Found: 2 C, 42.3; H, 3.2%; 3 C, 42.4; H, 3.3%; 4 C, 42.1; H, 3.1%: Spectroscopic data: IR and <sup>1</sup>H NMR see Table 1; <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 295 K) 3,  $\delta$  225.17 (Re-C(O)Ph), 200.11 (Re-CO), 130.59 (Ph, C para), 128.20, 127.01 (C ortho and meta), 109.2 (C ipso), 94.24  $(\text{Re-Cp}), -35.52(\text{Re-CH}_3); 4 \delta 204.18, 142.5, 130.17,$ 128.73, 126.40, 88.10, 28.06; see Table 4 for the low temperature spectra of the two isomers of 4.

### 3.1.2. Reaction at 273 K

A sample of Li<sup>+</sup>1 (87 mg, 0.21 mmol) was suspended in diethyl ether and the reaction flask was kept at 273 K. The suspension was treated with CF<sub>3</sub>SO<sub>3</sub>Me (28  $\mu$ l, 0.24 mmol) and stirred. IR monitoring showed completion of the reaction in 24 h approximately, to give a mixture constituted mainly by compounds **2**, **3**, and **4**, in a ratio comparable with that of the same reaction at r.t..

### 3.1.3. Reaction at 308 K

A sample of  $\text{Li}^+1$  (170 mg, 0.40 mmol) suspended in diethyl ether and treated with CF<sub>3</sub>SO<sub>3</sub>Me (56 µl, 0.49 mmol), was refluxed on a water bath at 310 K until IR monitoring showed completion of the reaction (75 min), to give a mixture of **2**, **3**, and **4**, in a ratio substantially comparable with that observed at r.t..

## 3.2. Reaction of $Li^+[Cp(CO)_2ReC(O)Ph]^-(Li^+1)$ with $CF_3SO_3Me$ in acetone

A sample of  $Li^+1$  (300 mg, 0.71 mmol) was suspended in 20 ml of acetone and treated at r.t. with  $CF_3SO_3Me$  (90 µl, 0.80 mmol). The mixture was stirred for 1.5 h. During the reaction the color changed from yellow to orange. IR monitoring revealed that **2** was largely dominant in the reaction mixture. Formation of **3** or **4** was not detected. Chromatographic separation on silica gel with 4:1 (v/v) *n*-hexane: diethyl ether afforded a dark orange fraction: the IR spectrum (*n*-hexane) showed the presence of **2** and of another unknown species, responsible for v(CO) bands at 1983sh, 1978s, 1907s cm<sup>-1</sup> and an <sup>1</sup>H resonance at  $\delta$  4.80 ppm (C<sub>6</sub>D<sub>6</sub>).

# 3.3. Reaction of $Li^+[Cp(CO)_2ReC(O)Ph]^-(Li^+1)$ with $CF_3SO_3Me$ in THF

A sample of Li<sup>+</sup>1 (15 mg, 0.036 mmol), was dissolved in THF (4 ml) and treated at 193 K with CF<sub>3</sub>SO<sub>3</sub>Me (5  $\mu$ l, 0.044 mmol). The solution was warmed up to r.t. and the color turned from yellow to orange. IR and NMR revealed the formation of 2 and 3 (ratio 2:1 ca.) and of a very small amount of 4 (ca. 5% of the reaction mixture).

# 3.4. Reaction of $Li^+[Cp(CO)_2ReC(O)Ph]^-(Li^+1)$ with $CF_3SO_3Me$ in cyclohexane

A sample of Li<sup>+</sup>1 (45 mg, 0.11 mmol), was suspended in cyclohexane (8 ml) and treated at r.t. with CF<sub>3</sub>SO<sub>3</sub>Me (13  $\mu$ l, 0.11 mmol). The mixture was stirred at r.t.. During the reaction time the color of the solution became pale red. The IR spectrum recorded after 2 h showed the formation mainly of 2 and 3 (ratio ca. 1:1), with minor amounts of 4 (ca. 10%).

# 3.5. Reaction of $Li^+[Cp(CO)_2ReC(O)Ph]^-$ with $(CH_3)_3OBF_4$ in diethyl ether

A sample of Li<sup>+</sup>1 (56 mg, 0.13 mmol) suspended in diethyl ether (6 ml) was treated at r.t. with  $(CH_3)_3OBF_4$ (23 mg, 0.15 mmol). The IR spectrum after 2.5 h showed the formation of 2 and 3 (ratio ca. 4:1) which were isolated by chromatography, as described above.

# 3.6. Reaction of $Li^+[Cp(CO)_2ReC(O)Ph]^-$ with $CH_3I$ in diethyl ether

A sample of Li<sup>+</sup>1 (33 mg, 0.079 mmol), suspended in diethyl ether (3 ml) was treated at r.t. with CH<sub>3</sub>I freshly distilled (14  $\mu$ l, 0.22 mmol) and stirred at r.t. for 3 days, protected from light. IR monitoring showed formation only of compound **3**.

# 3.7. Parallel alkylation reactions in the dark and in the light

Two Schlenk tubes were charged with the same amount of  $Li^+1$  (40 mg ca., 0.095 mmol), and suspended in freshly distilled diethyl ether (5 ml). One of the Schlenk tube was protected from light. Both the tubes were treated at r.t. with CF<sub>3</sub>SO<sub>3</sub>Me (12 µl ca., 0.10 mmol). The IR spectra recorded after stirring the mixtures for 2 h did not show any significant difference.

# 3.8. Reaction of $Li[Cp(CO)_2ReC(O)Me]$ with $CF_3SO_3Me$ in diethyl ether

A sample of CpRe(CO)<sub>3</sub> (50 mg, 0.15 mmol) in 5 ml of diethyl ether was treated with a 1.6 M CH<sub>3</sub>Li/THFcumene solution (120  $\mu$ l, ca. 0.19 mmol). After 2 h, the precipitate of Li[Cp(CO)<sub>2</sub>ReC(O)Me] [5] was isolated, dried, suspended in diethyl ether and treated at r.t. with CF<sub>3</sub>SO<sub>3</sub>Me (16  $\mu$ l, 0.14 mmol). After 2 h IR monitoring showed the formation mainly of [Cp(CO)<sub>2</sub>Re(Me)(COMe)], accompanied by a smaller amount (ca. 20%) of [Cp(CO)<sub>2</sub>Re{C(OMe)Me}].

### 3.9. Reaction of 4 with $CH_2Cl_2$

A sample of **4** (10 mg, 0.024 mmol) was dissolved at r.t. in CH<sub>2</sub>Cl<sub>2</sub> (3 ml ca.). IR monitoring showed the progressive decrease of the intensity of the carbonyl bands of **4**, substituted by new bands, attributable to [CpRe(CO)<sub>3</sub>] (2024 and 1926 cm<sup>-1</sup>), free acetophenone (1685 cm<sup>-1</sup>), and to the novel species [Cp(CO)<sub>2</sub>R-eCl(CH<sub>2</sub>Cl)] (**5**) (at 2042s and 1959vs cm<sup>-1</sup>). After 5 h the reaction went to completion. The NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, r.t.) showed the resonances of free acetophenone ( $\delta$  7.90–7.37, 2.51 ppm), of [CpRe(CO)<sub>3</sub>] ( $\delta$  5.34 ppm), and of **5**, at  $\delta$  5.85 (s, 5H), 4.72 (d, 1H), 4.49 (d, 1H,  $J_{H-H} = 9$  Hz) ppm.

### 3.10. X-ray data collection and structure refinement

A suitable crystal of 4 was mounted in air on a glass fibre tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at r.t.. Unit cell parameters were obtained from least-squares fitting of the setting angles of 25 randomly distributed intense reflections with  $10 \le \theta \le 14^\circ$ . Data collection was performed by the  $\omega$  scan method with variable scan speed (maximum time per reflection 70 s) and variable scan ranges  $(1.00+0.35 \tan \theta (^{\circ}))$ . Crystal stability under diffraction was checked by monitoring three standard reflections every 180 min. The measured intensities were corrected for Lorentz, polarization, decay, and background effects and reduced to  $F_o^2$ . An empirical absorption correction was applied using  $\psi$  scans of three suitable reflections having  $\chi$  values close to 90° [29]. Crystal data and data collection parameters are summarized in Table 5.

The structures were solved by direct methods [30] and subsequent Fourier synthesis; they were refined by fullmatrix least-squares on  $F^2$  using reflections with  $I > 2\sigma(I)$  [31]. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the internal library of SHELX97. Weights were assigned to individual observations according to the formula w = 1/2

Table 5 Summary of crystal data and structure refinement parameters for 4

| Formula                            | $C_{15}H_{13}O_3Re$                          |
|------------------------------------|--|
| Formula weight                     | 427.45                                       |
| Crystal system                     | monoclinic                                   |
| Space group                        | $P2_1/c$ (No. 14)                            |
| a (Å)                              | 12.172(3)                                    |
| <i>b</i> (Å)                       | 8.338(2)                                     |
| <i>c</i> (Å)                       | 14.856(2)                                    |
| β (°)                              | 112.46(2)                                    |
| V (Å <sup>3</sup> )                | 1393.4(5)                                    |
| Ζ                                  | 4  |
| F(000)                             | 808  |
| Density $(g \text{ cm}^{-3})$      | 2.038  |
| Absorption coefficient $(mm^{-1})$ | 8.721  |
| Crystal description                | red prism                                    |
| Crystal size (mm)                  | 0.26 	imes 0.21 	imes 0.14                   |
| $\theta$ Range (°)                 | $3.0 \le \theta \le 25.0$                    |
| Index ranges                       | $-14 \le h \le 13, \ 0 \le k \le 9, \ 0 \le$ |
|                                    | $l \leq 17$                                  |
| Intensity decay (%)                | 5  |
| Transmission factors (min, max)    | 0.186, 0.375                                 |
| Collected reflections              | 2437   |
| Reflections with $I > 2\sigma(I)$  | 2077   |
| Data/parameters                    | 2077/173                                     |
| Weights $(a, b)^{a}$               | 0.04, 1.17                                   |
| Goodness-of-fit $S(F^2)^{\rm b}$   | 1.115  |
| $R(F)^{c}$                         | 0.0243                                       |
| $WR(F^2)^{d}$                      | 0.0611                                       |
| Maximum difference peak, hole (e   | 0.758, -0.917                                |
| A <sup>-</sup> )                   |  |

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . <sup>b</sup>  $S = [\Sigma w (F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ , where *n* is the number of reflections and p is the number of refined parameters.

<sup>c</sup>  $R(F) = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$ <sup>d</sup>  $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ .

 $[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ; a and b were chosen to give a flat analysis of variance in terms of  $F_{\rm o}^2$ . Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in idealized position and refined riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent carbon atom. The hydrogen atoms of the methyl group has been modeled as disordered over two positions (with an occupation factor of 1/2 each) rotated from each other by  $60^{\circ}$ . Final difference electron density map showed no features of chemical significance, with the largest peaks lying close to the metal atom. Final conventional agreement indexes and other structure refinement parameters are listed in Table 5.

#### 4. Supplementary materials

A complete list of atomic coordinates, anisotropic displacement parameters, bond lengths and angles,

observed and calculated structure factors moduli for 4 (8 pages) are available from the authors on request.

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