From μ_3- to μ- Agostic Methyl Coordination: NMR and Solid State Study of Donor Ligands Uptake by the Triangular Cluster Anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}CH_3)(CO)_9]^-$.

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Dedicated to the memory of Professor Renato Ugo for his fundamental contribution to coordination and organometallic chemistry.

Abstract

$[Re_3(\mu\text{-}H)_3(\mu_3\text{-}CH_3)(CO)_9]^-$ (**1**) reacts with CO at 273 K to quantitatively give the $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_{10}]^-$ derivative (**2**) through the conversion of the methyl group from triply to doubly-bridging coordination. An NMR isotopic perturbation experiment demonstrates the unsymmetrical bridging of the methyl group on the Re-Re bond, and a fast exchange, in solution, between one agostic and two terminal C-H bonds. This is in agreement with X-Ray diffraction analysis performed on single crystals of **2**. In solution at room temperature **2** decomposes with CH_4 elimination, which is also observed when **2** is treated with CO affording the $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ anion. The opening of the triple bridging methyl coordination in **1** occurs also with other different L ligands, yielding to the *syn* and *anti* isomers of unsymmetrically bridged methyl complexes of general formula $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9(L)]^-$ (L = MeCN, $PMePh_2$, THF). The kinetic and thermodynamic stabilities of these isomers vary with the nucleophilicity of the ligand and the polarity of the solvent. In particular, the strong nucleophile $PMePh_2$ affords the quantitative conversion of anion **1** into the thermodynamic *syn* isomer, which is stable in THF at room temperature for several days. On the contrary, weak nucleophiles, such as MeCN or THF, give

equilibrium mixtures containing residual amounts of anion **1**. The adducts with MeCN are stable in solution at room temperature for several hours, while decompose fastly in neat MeCN affording mainly the cluster anion $[Re_3(\mu\text{-}H)_4(CO)_9(MeCN)]^-$. This suggests that cluster stabilization after methane evolution follows a different path with respect to that observed in the reaction of **1** with CO.

1. Introduction

~~The study of t~~The nature of metal-ligand interactions is of paramount importance in understanding the structure and the reactivity of inorganic and organometallic complexes, as well as in clarifying the mechanism for the synthesis of a great number of organic compounds. Accordingly, methyl- and other alkyl-bridged complexes are species of interest [1] and the knowledge of their interactions ~~of these groups~~ with transition metals can shed light on *i*) the C-H bond activation processes at a multimetal site [2], *ii*) the chemisorption of these groups on metal surfaces [3], *iii*) the subsequent catalysed reactions, such as the heterogeneous Fischer-Tropsh synthesis [4] and the homogeneous polymerization of ~~the~~ olefins [5]. ~~Hence,t~~ Transition metal-catalyzed C–H activation is then a topic of great interest which is well documented in the literature. ~~became one of the hottest topics in chemistry in the 21st century, and many reviews in this field have been published, including a special issue of Chemical Reviews in 2017~~ [6].

In this framework, we previously reported the synthesis and ~~the~~ full characterization of the anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}CH_3)(CO)_9]^-$ (**1**) [7], which provides a unique example of a methyl group symmetrically bridging on three metal atoms, with C_{3v} symmetry (Chart 1). The methyl group was obtained by insertion of methylene (generated from diazomethane) into the $Re_3(\mu_3\text{-}H)$ moiety of the "super unsaturated" anion $[Re_3(\mu_3\text{-}H)(\mu\text{-}H)_3(CO)_9]^-$ (44 valence electrons) [8].

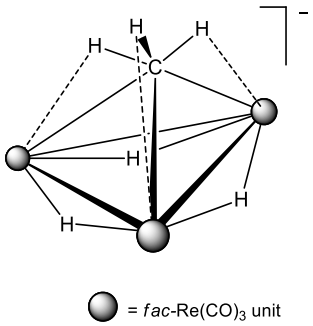


Chart 1. A view of the anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}CH_3)(CO)_9]^-$ (**1**).

The anion **1**, fully characterised in the solid-state through X-ray analysis, is stable in solution even at room temperature, allowing an extensive spectroscopic characterisation that confirmed the maintenance of the solid-state structure also in solution. Theoretical calculations and several pieces of experimental evidence (the eclipsed location of the methyl hydrogens with respect to the C_{Me}-Re bonds, the chemical shift value of these hydrogens and ^1H relaxation times) indicated the occurrence of both σ and π donations from the methyl to the cluster moiety, giving rise to some degree of agostic character [9] for the three C-H···Re interactions.

The high stability of **1** is likely due to the presence of bridging ligands on all the Re-Re interactions of the triangular cluster, which removes the possibility of C-H activation through multiple oxidative additions (equation 1), as observed in previous examples of cluster bound methyl groups, such as $[Fe_3(\mu\text{-}H)(\mu_3\text{-}H_2CH)(CO)_9]$ [10] or $[Os_3(\mu\text{-}H)(\mu\text{-}HCH_2)(CO)_{10}]$ [11] and as postulated in processes of methane activation over metal surfaces [12].

$$M\text{-}CH_3 \rightarrow M(H)CH_2 \rightarrow M(H)_2CH \qquad (1)$$

Moreover, the bridging location of both CH_3 and hydrides hampers the reductive elimination of CH_4, while generally alkyl-hydrido complexes are unstable towards this reaction.

The absence of methane elimination prompted us to investigate the occurrence of insertion reactions upon treatment of anion **1** with donor ligands, able to promote the opening of the symmetric CH_3-Re_3 interactions. We report here the results obtained by reacting **1** with ligands of very variable donor strength, which show the formation of new triangular cluster anions of general formula $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9L]^-$ (L = CO, $PMePh_2$, MeCN, THF) containing a methyl group

bridging on two metal centres instead of three. Only a few examples of bridging methyl groups on two metal centres displaying a metal-metal bond are reported, [13] whose reactivity has not been explored in detail. Hence we were encouraged to study the structure (both in solution and solid-state) and the reactivity of these new triangular rhenium methyl complexes. In particular, we investigated the presence of a possible asymmetrical μ-CH_3 bridge, where one of the C-H bonds is involved in an agostic interaction with one of the rhenium centres, and the stability of this fragment towards the reductive elimination of methane.

2. Experimental

2.1. General procedures. All the manipulations were performed under nitrogen using oven-dried Schlenk-type glassware. The solvents, including THF-d_8 (Cambridge Isotope Laboratories®), were dried and de-oxygenated by standards methods before use, while CD_2Cl_2 (Cambridge Isotope Laboratories®) was used as received. The [PPh_4] salt of anion **1** was prepared as published [7]. $PMePh_2$ (99%) was purchased from Aldrich and stored under N_2. FT-IR spectra were acquired on a Bruker Vector22 FT spectrometer. The NMR spectra were acquired on Bruker AVANCE DRX-300, AC-200 or WP80 spectrometers. The temperature was calibrated with a standard CH_3OH/CD_3OD solution [14]. The ^1H T_1 values were obtained by using a standard inversion recovery pulse sequence of the Bruker library (t1ir), whose fitting afforded the T_1 values for each signal. GLC analyses were performed on Carlo Erba HRGC 5300.

Safety warning: The reactions with CO (SIAD) were performed working under a fume hood in a lab equipped with a detector of CO leaks

*2.2. Reaction of [PPh_4]**1** with CO in CD_2Cl_2 to form compound **2**.* The reaction was carried out directly in an NMR tube with a screw cup, dissolving [PPh_4]**1** (9.0 mg, 0.0077 mmol) in CD_2Cl_2 (0.5 mL). The solution was cooled to 193 K and CO (1 mL, measured at room temperature and atmospheric pressure, ca. 0.044 mmol) was introduced through the rubber septum of the cup. The sample was then maintained for about three minutes at room temperature observing the yellow colour of the solution turning pale. The reaction was then quenched at 193 K and a ^1H NMR

spectrum recorded immediately after showed only the hydrido signals of anion **2**. Slow diffusion of *n*-hexane into the dichloromethane solution of [PPh_4]**2** afforded single crystals suitable for X-ray analysis. FT-IR, ν(CO) (CH_2Cl_2, cm^{-1}): 2093w, 2024mw, 1995s, 1941mw, 1917sh, 1898mbr. ^{1}H NMR (CD_2Cl_2, 7.1 T): at 193 K δ -3.22 (s, 3H, CH_3), -10.57 (s, 1H, H_a), -15.83 (s, 2H, H_b); at 298 K δ -3.24 (s, 3H, CH_3), -10.42 (s, 1H, H_a), -15.69 (s, 2H, H_b). ^{13}C NMR (CD_2Cl_2, 7.1 T, 193 K) δ 189.3 (2 CO), 188.5 (2 CO), 185.8 (1 CO), 184.7 (2 CO), 182.5 (1 CO), -49.97 (μ-CH_3). Yield 63% (estimated by the ^{1}H NMR integrated intensities of the aromatic signals of PPh_4^+ counter ion as internal standard before and after the addition of CO).

2.3. X-ray Diffraction Structural Analysis. Crystal data for [PPh_4]**2**: $C_{35}H_{26}O_{10}PRe_3$, M_r = 1196.13, monoclinic, space group $P2_1/c$ (No. 14), a = 7.768(1), b = 31.080(5), c = 15.272(2) Å, β = 91.11(1)°, V = 3686.4(9) Å^3, Z = 4, d_{calc} = 2.155 g cm^{-3}, T = 193(2) K, crystal size = 0.260 × 0.220 × 0.100 mm^3, μ = 9.923 mm^{-1}, λ = 0.71073 Å. Refinement of 453 parameters on 8474 independent reflections out of 37177 measured reflections (R_{int} = 0.0525, $R_σ$ = 0.0459, $2θ_{max}$ = 56.7°) led to R_1 = 0.0346 ($I > 2σ(I)$), wR_2 = 0.0558 (all data), and S = 1.096, with the largest peak and hole of 1.734 and −1.164 e Å^{-3}. The structure has been refined employing anisotropic displacement parameters for all the non-hydrogen atoms. All the hydrogen atoms have been clearly seen in a difference Fourier map and later variously idealized. The hydrogen atoms of the agostic methyl ligand have been refined with a common isotropic displacement parameter. In order to maintain a local threefold symmetry for the methyl group, soft restrain on the three C–H distances (and the three H···H 1,3 interactions) has been implemented. Hydrido ligands have been placed in calculated positions [15] and refined with a common isotropic displacement parameter. Hydrogen atoms of the tetraphenylphosphonium cation have been added in idealized positions and refined riding on their parent atom with an isotropic displacement parameter 1.2 times that of the pertinent carbon atom. CCDC 2095598 contains the supplementary crystallographic data for the paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

*2.4. NMR experiment of isotopic perturbation of the equilibrium resonances on [PPh$_4$]**2***. The above described reaction was carried out in an NMR tube using a partially deuterated sample of [PPh$_4$]**1** (about 20 mg, 0.015 mmol~~s~~, obtained by a literature method [7]) dissolved in CD_2Cl_2 (0.5 mL). Variable temperature ^{1}H NMR spectra were acquired from 193 K to 283 K. Table S2 in the Supporting Information reports the averaged δ values for the three CH_3, CH_2D and CHD_2 isotopomers of the methyl ligand. Table S3 shows the δ_b, δ_t and the **A** values that were calculated solving the following equations, at the five different investigated temperatures:

$\delta(CH_3) = (2\delta_t + \delta_b) / 3$,

$\delta(CH_2D) = (\delta_t + \mathbf{A}\delta_t + \delta_b) / (\mathbf{A} + 2)$,

$\delta(CHD_2) = (2\mathbf{A}\delta_t + \delta_b) / (2\mathbf{A} + 1)$

*2.5. Stability of [PPh$_4$]**2** in CD_2Cl_2 at room temperature in the presence of CO.* A solution containing [PPh$_4$]**2** (9.0 mg, 0.0075 mmol) in CD_2Cl_2 (0.5 mL) was treated with CO (1 mL, about 0.044 mmol) at room temperature and the decomposition of **2** was monitored by ^{1}H NMR spectroscopy for about 70 min. Then, another aliquot~~e~~ of CO was ~~further~~ added to the solution (2 mL, ca. 0.088 mmol) and the reaction was followed by ^{1}H NMR for another 110 min at room temperature. To further promote the decomposition of **2**, the solution was placed under a CO atmosphere and the course of the reaction was monitored for another 100 min, affording a reaction mixture that mainly contains: a residual amount of anion **2** (4.6%); the anion $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ (59%); the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}]^-$ (8%) and the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OH)(CO)_{10}]^-$ (16%). ^{1}H NMR data (CD_2Cl_2, 298 K): [PPh$_4$][$Re_3(\mu\text{-}H)_3(\mu\text{-}Cl)(CO)_{10}$] δ -10.57 (s, 1H), -14.22 (s, 2H); [PPh$_4$][$Re_3(\mu\text{-}H)_3(\mu\text{-}OH)(CO)_{10}$] δ -9.43 (s, 1H), -13.74 (s, 2H).

*2.6. Reaction of [PPh$_4$]**1** with MeCN to form the isomers [PPh$_4$]**4a** and [PPh$_4$]**4b**.* The reaction was carried out many times directly in screw cup NMR tube in CD_2Cl_2, according to the following general procedure. An accurately weighed amount of [PPh$_4$]**1** (ca. 0.01 mmol) was dissolved in 0.6 mL of CD_2Cl_2. Then, the solution was cooled to 193 K and the selected volume of MeCN

(measured by a microsyringe) was introduced through the rubber septum of the tube, which was briefly shaken at room temperature and immediately introduced in the thermostated NMR probe. A sequence of automatic acquisition of the spectra started within 5 min after the mixing of the reagents. In the experiment shown in Fig. 4, 13.4 mg of [PPh_4]**1** (0.0115 mmol) were added with 11.8 µL (19.7 equivalents) of MeCN and a series of ^{1}H NMR spectra was acquired at 263 K at programmed times. The same procedures were followed for all the kinetic experiments described in the text. For the experiment of Fig. 6, 8.0 mg of [PPh_4]**1** (0.00686 mmol) were treated with increasing volumes of MeCN (3, 7, 17, 31 µL) and the ^{1}H NMR spectra were acquired at 300 K after each addition. For investigating the effect of the temperature on the equilibrium constants (Table 2, Fig. 7 and 8), 12.3 mg of [PPh_4]**1** (0.0105 mmol) were treated with 10.8 µL (19.7 equivalents) of MeCN at 193 K, and a series of ^{1}H NMR spectra was acquired at 273 K, until the equilibrium was attained. Without extracting the tube from the magnet, the temperature was increased and the procedure was repeated at three more temperatures (283, 293, and 303 K). Isomer **4a**: ^{1}H NMR (CD_2Cl_2, 7.1 T, 193 K) δ 1.26 (s, 3H, *CH*$_3$CN), -3.23 (s, 3H, µ-CH_3), -10.34 (s, 1H, H_a), -13.89 (s, 2H, H_b). Isomer **4b**: ^{1}H NMR (CD_2Cl_2, 7.1 T, 193 K) δ 2.31 (s, 3H, *CH*$_3$CN), -3.39 (s, 3H, µ-CH_3), -10.27 (s, 1H, H_a), -13.37 (s, 2H, H_b). Yield 84% (estimated by the ^{1}H NMR integrated intensities of the aromatic signals of PPh_4^+ counter ion as internal standard before and after the addition of MeCN).

*2.7 Reactions of [PPh_4]**1** with PPh_2Me to afford the isomers [PPh_4]**5a** and [PPh_4]**5b**.* A sample of [PPh_4]**1** (9.9 mg, 0.0085 mmol) was dissolved in THF-d_8 (0.6 mL) at 193 K directly in an NMR tube, and treated with 1 equivalent (1.7 µL) of $PMePh_2$. The sample was shaken and maintained at room temperature for 5 min, then ^{1}H and ^{31}P NMR spectra were acquired at 193 K. The sample was extracted from the magnet and maintained at room temperature for different times, followed by the acquisition of novel spectra at 193 K (Fig. S7). Finally, the tube was maintained at room temperature for 68 h, after which ^{1}H and ^{31}P NMR spectra were acquired at room

temperature and the heteronuclear nOe experiment described in the Results and Discussion paragraph was performed.

Isomer **5a**: ^{1}H NMR (CD_2Cl_2, 7.1 T, 193 K) δ 7.58 (m, $2H_{para}$, PMe*Ph*$_2$), 7.49-7.22 (m, $8H_{ortho\text{-}meta}$, PMe*Ph*$_2$), 2.29 (d, 3H, P*Me*$(C_6H_5)_2$, J_{HP} 7.95 Hz), -2.69 (s, 3H, CH_3), -10.37 (s, 1H, H_a), -15.28 (d, 2H, H_b, J_{HP} 12 Hz). ^{31}P NMR (THF, 7.1 T, 193 K) δ –13.6. Isomer **5b**: ^{1}H NMR (CD_2Cl_2, 7.1 T, 193 K) δ 7.65 (m, $2H_{para}$, PMe*Ph*$_2$), 7.49-7.22 (m, $8H_{ortho\text{-}meta}$, PMe*Ph*$_2$), 2.34 (d, 3H, P*Me*$(C_6H_5)_2$, J_{HP} 7.84 Hz), -3.66 (s, 3H, CH_3), -10.07 (s, 1H, H_a), -14.64 (d, 2H, H_b, J_{HP} 16 Hz); ^{13}C NMR (CD_2Cl_2, 9.4 T, 298 K) δ 195.3 (2 CO), 191.4 (2 CO), 190.5 (2 CO), 189.8 (2 CO), 187.5 (1 CO), 132-128 (PMe*Ph*$_2$), 0.73 (P*Me*Ph$_2$), -50.9 (μ-CH_3). ^{31}P NMR (THF, 7.1 T, 193 K) δ –19.7. Yield > 95% (estimated by the ^{1}H NMR integrated intensities of the aromatic signals of PPh_4^+ counter ion as internal standard before and after the addition of $PMePh_2$).

*2.8 Reactions of [PPh$_4$]**1** with THF*. A sample of [PPh_4]**1** (7.5 mg, 0.063 mmol) was dissolved at room temperature in 0.6 mL of THF-d_8. ^{1}H NMR spectra were acquired every 30 minutes, showing the decrease of the concentration of **1**. ^{1}H NMR (CD_2Cl_2, 7.1 T, 193 K) δ -3.38 (s, 3H, μ-CH_3), -9.50 (s, 1H, H_a), -10.88 (s, 2H, H_b).

3. Results and discussion

*3.1. Reaction with carbon monoxide: the novel anion [Re$_3$(μ-H)$_3$(μ-CH$_3$)(CO)$_{10}$]$^-$ (**2**).* The addition of carbon monoxide to a CH_2Cl_2 solution of [PPh_4]**1** causes the clean conversion of **1** into $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_{10}]^-$ (**2**), as indicated by the ^{1}H NMR monitoring at 273 K (Fig. 1). Three high-field signals are observed, with integrated intensities in the ratio 3:1:2 (see Table 1), attributable to the methyl hydrogens and the hydrides H_a and H_b, bridging the base and the lateral edges of the triangular cluster, respectively.

The significant shielding of the ^{1}H methyl resonance (–3.22 ppm) suggests the presence of an agostic interaction, as observed in other dinuclear complexes having CH_2R bridges over transition

metal centres. [13a, 13c, 16] A high field resonance is observed also in the ^{13}C NMR spectrum (–49.97 ppm) (Fig. S1) [17, 18]. A 2D ^{1}H-^{13}C modified HMQC correlation experiment [19] confirms that this is the signal of the carbon atom bearing the three agostic hydrogens (Fig. S2).

The ^{1}H and ^{13}C NMR data (two hydrido signals in the ratio 1:2, six carbonyl resonances, in the ratio 1:1:2:2:2:2, see Figs S1 and S3 for the carbonyl attributions) agree with a C_s symmetry of the anion **2**. This symmetry likely results from a fast fluxional process equalizing one agostic and two terminal C-H bonds, as depicted in Scheme 1. This process is fast enough to give an averaged signal even at low temperatures. The dynamic process gives rise also to an averaged ^{1}H-^{13}C coupling constant ($^{1}J_{CH}$ =116 Hz), whose value falls between those typical for sp^3 C atoms (e.g. 125 Hz for methane) and those typical for agostic interactions ($^{1}J_{CH}$ in the range 75-100 Hz) [9b,c]. The dynamic nature of the observed C_s symmetry has been further demonstrated through an experiment of isotopic perturbation of the equilibrium by partial deuteration, analogous to that carried out for the above-quoted Os_3 cluster containing a doubly bridging methyl group [11, 20].

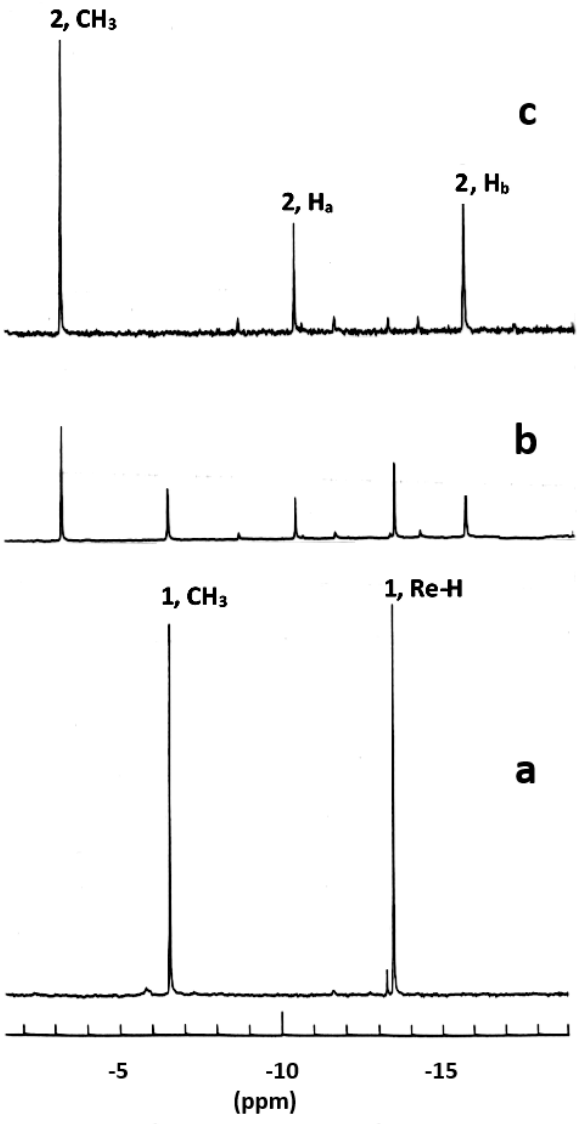
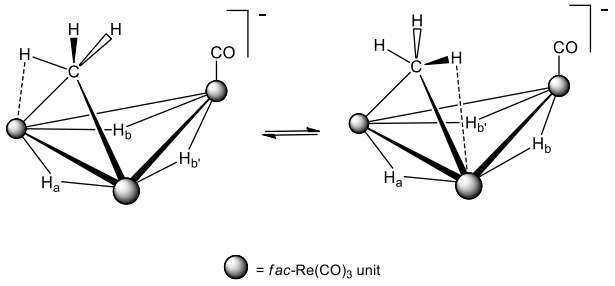


Fig. 1. Hydride region of ^{1}H NMR spectra (CD_2Cl_2, 273 K, 1.9 T) while monitoring the reaction of [PPh_4]**1** with CO, directly in the NMR tube: a) before CO addition; b) after a few minutes; c) at the end of the reaction.



Scheme 1 The dynamic process giving the apparent C_s symmetry observed in anion **2**.

We have therefore prepared a partially deuterated sample of **2**, by reacting with CO a partially deuterated sample of **1**, obtained using deuterium-enriched diazomethane. The ^{1}H NMR spectrum

of this sample shows three methyl signals for the three CH_3, CH_2D and CHD_2 isotopomers (Fig. 2). The assignment of the resonance at δ –3.219 to the CH_3 isotopomer is straightforward when compared with the signal of the sample not containing deuterium. Moreover, the relative trends at 213 K both of the T_1 values of the three signals (from left to right in Fig. 2: 455 ms, 711 ms, and 1971 ms) and of the half-height linewidths (Table S1 in Supporting Information) indicate that the high-field shift corresponds to a progressive increase of the deuterium content in the isotopomers.

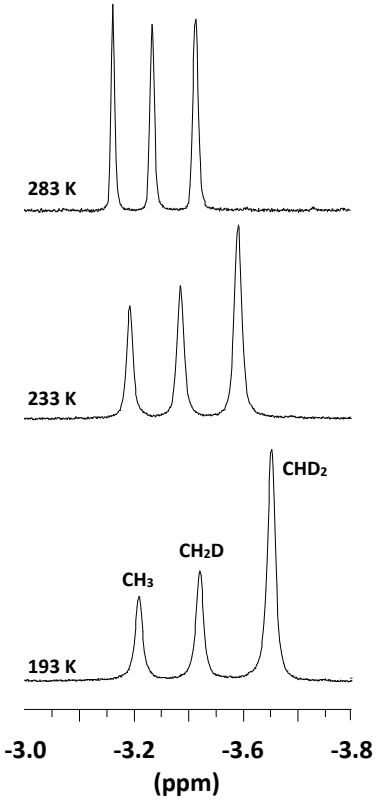


Fig. 2. Variable temperature ^{1}H NMR spectra showing the resonances of the methyl group in a partially deuterated sample of compound **2**, showing the increase of the Δδ between the signals of the three isotopomers and their differential broadening (H_3 > H_2D > HD_2, Table S1) on decreasing the temperature.

The direction and the extent of the resonance shifts of the deuterated isotopomers can be explained taking into account that ^{2}H atoms preferentially locate in the classical CH sites, due to their preference for stiffer bonds [21], leaving ^{1}H atoms more concentrated in the upfield-shifted agostic locations. Therefore, as the ^{2}H content increases, in the CH_3, CH_2D, CHD_2 series, the corresponding ^{1}H signal progressively shifts to higher fields (Fig. 2). Since the resonance of each isotopomer is averaged from the fast exchange between C-H and C-H-Re sites and, on decreasing

the temperature, the equilibrium between the two sites progressively shifts towards the more stable form (i.e. the one with ^1H in the agostic site), a significant temperature-dependent isotope shift (Table S2), as well as a broadening of the three CH_3, CH_2D, CHD_2 isotopomer resonances is observed (Table S1). For instance, $\Delta\delta$ for $\delta(CH_3)$ - $\delta(CH_2D)$ passes from 0.154 ppm at 283 K to 0.223 ppm at 193 K, and $\Delta\delta$ for $\delta(CH_2D)$ - $\delta(CHD_2)$ from 0.171 ppm to 0.262 ppm, in the same temperature range [22].

It is worth noticing that in the parent compound **1** the $\Delta\delta$ between the resonances of the CH_3, CH_2D, and CHD_2 isotopomers were much smaller (about 0.035 ppm, of the same order of magnitude of geminal deuterium isotopic effects [23]) and did not show the increase with a lowering of the temperature typical of fluxional systems [7]. This evidenced a true C_{3v} symmetry of **1** deriving from the symmetric triple-bridging methyl coordination involving three C-H-Re interactions and not from a dynamic process as that observed in anion **2**.

According to Shapley *et al.* [11b], the position of the CH_3, CH_2D and CHD_2 resonances can be expressed in terms of three parameters: the chemical shifts of the terminal (C-H, δ_t) and of the bridging (C-H-Re, δ_b) methyl hydrogen atoms, and the *A* parameter [$A = \exp(-\Delta E/RT)$] that indicates the different population of the various conformers on the bases of their energy differences (see Experimental). Solving the three equations at each temperature, the values of the three parameters have been estimated, the mean results being $\delta_b = -8.93 \pm 0.16$ ppm, $\delta_t = -0.31 \pm 0.11$ ppm, $\Delta E = 390 \pm 13$ J mol^{-1}. The δ values are closely comparable to those found for the related $[Re_2(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_8]$ complex ($\delta_b = -8.31$, $\delta_t = -0.16$, $\Delta E = 645 \pm 10$ J mol^{-1}) [24], and to those reported for complexes having asymmetrical agostic methyl bridges [11b,c], thus confirming the reliability of the results [25].

3.2. Solid state structure. The structure of anion $[Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_{10}]^-$, as determined by X-ray diffraction in a crystal of its $[PPh_4]^+$ salt at 193 K, is depicted in Fig. 3. It contains an approximately isosceles triangle of metal atoms with an edge bridged by a methyl ligand

asymmetrically coordinated. The two rhenium atoms of the bridged edge bear one axial and two equatorial carbonyl ligands each. The rhenium atom of the non-bridged vertex is bound to the remaining four carbonyl ligands, two axial and two equatorial. The three hydrido ligands bridge the three rhenium-rhenium edges on the side of the molecule opposite to the one occupied by the methyl ligand. The rhenium-hydrogen bonds occupy positions approximatively *trans* to the equatorial carbonyl ligands. Leaving apart metal-metal interactions, and assuming that the bond C(1)–H(12) of the methyl group interacting with Re(2) occupies a coordinative position, the coordination geometry around the three metal atoms can be idealized as octahedral.

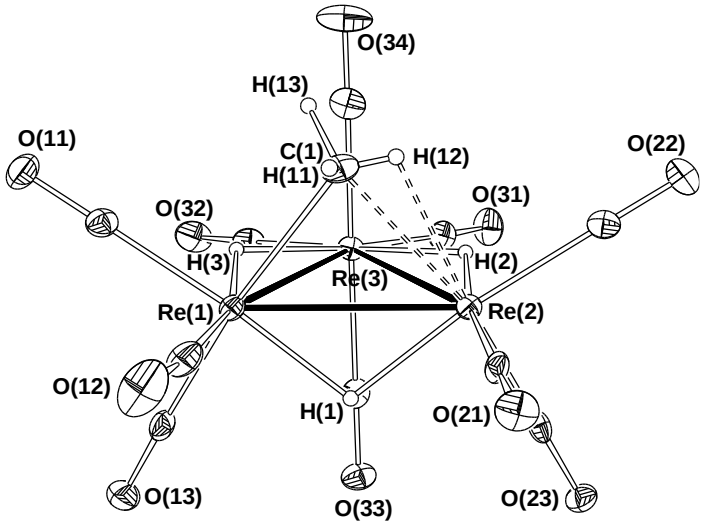


Fig. 3. ORTEP plot of the anion $[Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_{10}]^-$ (**2**) with a partial labelling scheme.

The carbon atom of the bridging methyl group is asymmetrically coordinated to the two rhenium atoms: distance Re(1)–C(1), 2.317(6) Å, is significantly longer than a typical Re–C_{Me} distance found for terminal methyl ligands (mean value 2.172 Å)[26], and distance Re(2)–C(1), 2.444(5) Å, is even longer than the Re–C_{Me} distance found in the previously reported complex $[Re_3(\mu_3\text{-}CH_3)(\mu\text{-}H)_3(CO)_9]^-$ (2.401 Å). [7]

One of the C–H bonds of the methyl group is found to be eclipsed with respect to the longer Re–C_{Me} interaction. As a consequence, the corresponding hydrogen atom~~s~~ H(12) lies at only 2.12(6) Å from atom Re(2). The midpoint of this C–H bond occupies a *trans* position with respect

to the axial carbonyl ligand bound to Re(2). These observations are in agreement with an agostic description for the C(1)–H(12)···Re(2) interaction.

Leaving apart the clearly asymmetric coordination of the methyl ligand, the coordination geometry of the two rhenium atoms of the bridged edge is surprisingly similar so that, as a whole, the anion only slightly departs from an idealized C_s symmetry (see Fig. 3).

Taking into account the presence of an agostic interaction, by which the methyl ligand become a formal three-electron donor, anion $[Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_{10}]^-$ (**2**) should be considered electronically saturated. The mean rhenium-rhenium distance for the edges not bridged by the methyl group is 3.220 Å, indeed quite similar to the mean distance of 3.241 Å found in the saturated species $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ [27].

*3.3. The stability of the derivative $[Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_{10}]^-$ (**2**).* The stability of the anion **2** in solution is much lower than that of the parent anion **1** so that most of the spectroscopic characterizations have been carried out at low temperature. Indeed, anion **1** is stable in CD_2Cl_2 at room temperature over several days. On the contrary, ^{1}H NMR monitoring of a CD_2Cl_2 solution of **2** at room temperature reveals decomposition of ca. 85% over only 3 h, to give several hydrido derivatives which have been only partially identified (see Experimental). The most intense signals are attributable to the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OH)(CO)_{10}]^-$ (**3**), arising most likely from the protonation of the methyl group by adventitious water (the simultaneous appearance of the signal of methane is observed, at δ 0.24). However, the classical mechanism of reductive elimination of CH_4, promoted by water coordination and its successive oxidative addition, cannot be ruled out for the formation of anion **3**. Methane evolution is also observed ~~also~~ upon treatment of compound **2** with CO. The reaction leads to the formation of the dihydrido derivative $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$, accordingly to the classical mechanism of reductive elimination of CH_4, promoted by ligand addition on hydrido-alkyl complexes (equation 2). The reaction is rather slow, even under 1 atm of CO (see Experimental). ^{1}H NMR monitoring in the presence of a lower CO concentration shows

also the competitive formation of some species deriving from the decomposition of **2** in the absence of CO (such as the ~~protonation~~ hydroxo derivative **3** due to the presence of ~~by~~ adventitious water). No evidence of any other molecule or fragment containing a methyl group is obtained, indicating that evolution as methane is the only fate of the bridging methyl group.

$$[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_{10}]^- + 2\ CO \rightarrow [Re_3(\mu\text{-}H)_2(CO)_{12}]^- + CH_4 \quad (2)$$

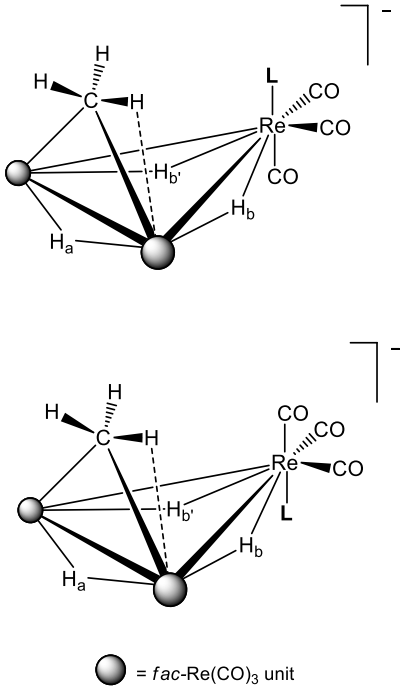
Reasonably, the first step of this reaction is the opening of the agostic interaction in **2** by CO coordination, to give the intermediate $[Re_3(\mu\text{-}H)_3(CH_3)(CO)_{11}]^-$ containing a terminally bound methyl group. This complex has not been detected by ^1H monitoring, implying that methane elimination from this species is faster than CO coordination on **2**.

*3.4. Reaction of **1** with acetonitrile (MeCN): the two isomers of $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9(NCMe)]^-$ (**4**).* The ability of a relatively weak donor ligand such as MeCN to open the triple bridging coordination of the methyl group is also investigated, observing a somewhat different behaviour. Upon treatment with an excess (10 equivalents) of MeCN at room temperature, the resonances of **1** are progressively replaced by two sets of three signals (ratio 3:1:2), at chemical shifts similar to those of **2** (see Fig. 4 and Table 1). These signals can be easily attributed to the *syn* and *anti* isomers of the addition product $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9(NCMe)]^-$ (**4b** and **4a**, respectively, equation 3 with L = MeCN), in which one MeCN ligand is axially coordinated on the vertex not involved in ~~of the cluster opposite to~~ the Re-(μ-CH_3)Re ~~basal~~ interaction (Scheme 2).

$$[Re_3(\mu_3\text{-}CH_3)(\mu\text{-}H)_3(CO)_9]^- + L \rightleftarrows [Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_9L]^- \quad (3)$$

Table 1 ^{1}H NMR data (δ, ppm) for the methyl and hydride signals of the $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9L]^-$ complexes here described, at 193 K, 7.1 T, in CD_2Cl_2 (**2** and **4**) or THF-d_8 (**5** and **6**).

L	Compound	μ-CH_3	H_a	H_b
CO	**2**	-3.22	-10.57	-15.83
MeCN	**4a**	-3.23	-10.34	-13.89
MeCN	**4b**	-3.39	-10.27	-13.37
$PMePh_2$	**5a**	-2.69	-10.37	-15.28 (d, J_{HP} 12 Hz)
$PMePh_2$	**5b**	-3.66	-10.07	-14.64 (d, J_{HP} 16 Hz)
THF	**6**	-3.38	-9.50	-10.88



Scheme 2. The *syn* and *anti* isomers of the addition derivatives $[Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_9L]$.

In both isomers, the resonances of the hydrides H_b show the downfield shift always observed in hydrido-carbonyl clusters of rhenium upon replacement of a carbonyl by a nitrile ligand in *cis* position on a $HRe(CO)_4$ vertex [28]. The close similarity of the chemical shift of the methyl resonances of **4a** and **4b** with that of the CH_3 group in **2** suggests an analogous coordination mode for the bridging methyl group. Moreover, the magnetic equivalence of the methyl hydrogens and the two H_b hydrides in both the isomers indicates an apparent C_s symmetry and ~~therefore~~ the occurrence, also in **4**, of a dynamic process equalizing the CH_3 protons.

A 2D NOESY experiment indicates unambiguosly that **4b** is the *syn* isomer, since the methyl resonance of coordinated acetonitrile exhibits a cross-peak correlation with the methyl signal of **4b** and not with that of **4a** (Fig. S4 in Supporting Information).

The progress of the reaction has been monitored by ^{1}H NMR directly in an NMR tube, and Fig. 4 shows the time evolution of the spectra for an experiment at 263 K, in the presence of 19.7 equivalents of MeCN.

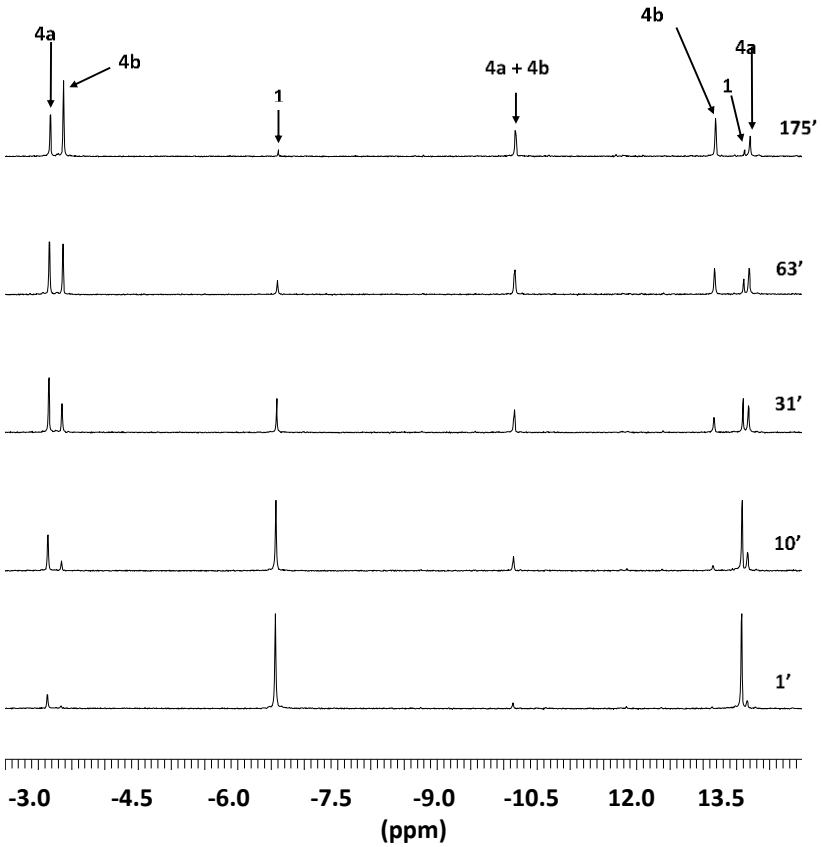


Fig. 4: ^{1}H NMR monitoring over time of the transformation of **1** into the equilibrium mixture **4a**/**4b**, in CD_2Cl, at 263 K in the presence of 19.7 equivalents of MeCN.

From the integrated intensities of the hydridic signals, the composition of the reaction mixtures at different times has been calculated and depicted in Fig. 5.

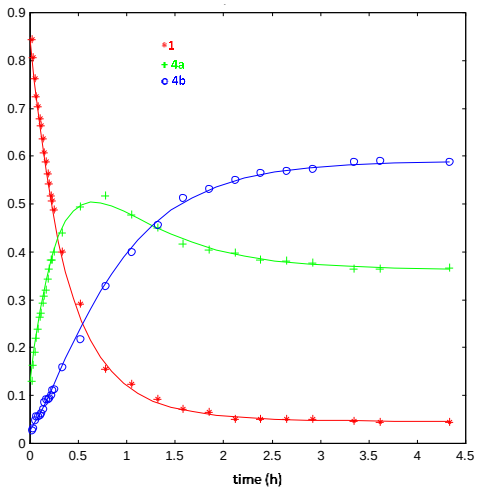


Fig. 5. Time evolution of the concentrations of the reactant **1** and the two isomers **4a** and **4b**, estimated from the integrated intensities in the ^{1}H NMR spectra recorded in the experiment at 263 K, with 19.7 equivalents of MeCN (selected spectra are shown in **Fig 4**).

The isomer **4a** is the main product at the initial reaction stages, its concentration attains a maximum (at ca. 50% of conversion, in this case) and subsequently the isomer **4b** becomes the dominant product. Noteworthy, a residual amount of **1** is always present at the end of the reaction, indicating that, unlike the reaction with the strong ligands CO and $PMePh_2$ (see below), the equilibrium 3 in the case of MeCN is not completely driven to the right, even in the presence of a large excess of the MeCN ligand.

In line with this, the ratio between the overall equilibrium concentrations of the two isomers **4a** and **4b** and that of **1** linearly increases on increasing the MeCN concentration, as shown in Fig. 6 for an experiment at 300 K. From the slope of the straight line a value of the pseudo equilibrium constant K_{app} = 9.9(2) can be estimated, according to equation 4.

$$K_{app} = \frac{[4a + 4b]}{[1][MeCN]} \qquad (4)$$

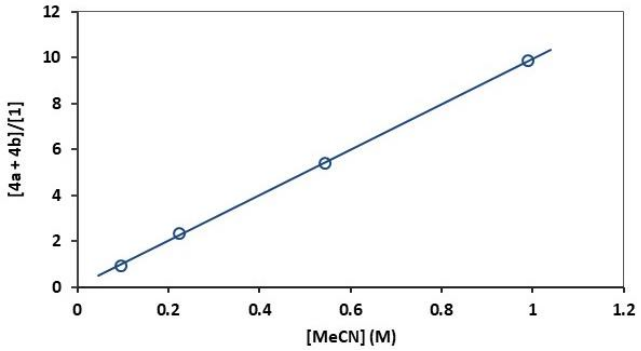


Fig. 6. The increase of the [**4a** + **4b**]/[**1**] ratio on increasing [MeCN], at 300 K in CD_2Cl_2 solution.

The observed course of reaction 3 (Fig. 5) suggests the occurrence of the two reversible consecutive steps (equations 5a and 5b), ruled by the equilibrium constants K_1 and K_2, respectively, with the above K_{app} corresponding to $(K_2 + 1)\times K_1$.

1 + MeCN ⇄ **4a** (5a)

4a ⇄ **4b** (5b)

Experiments at different temperatures show that the equilibrium concentration of the unreacted **1** increases on increasing the temperature (Fig. 7), as expected for an associative equilibrium (5a). From Fig. 7 it is also clear that the [**4b**]/[**4a**] ratio (i.e. K_2) decreases with the temperature. The values of K_1 and K_2 estimated at different temperatures have been reported in Table 2.

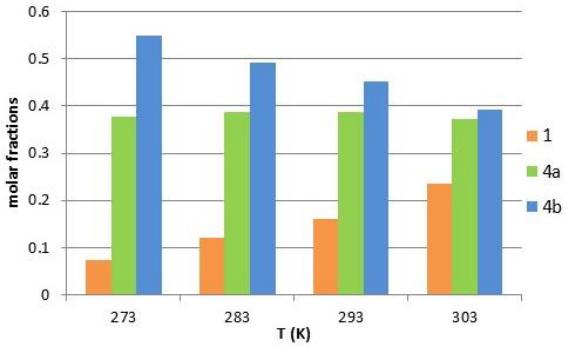


Fig. 7. Variation of the equilibrium concentrations of **1**, **4a** and **4b** at different temperatures, in the presence of 20 equivalents of MeCN.

From the corresponding Van't Hoff plots (Fig. 8) the values of the thermodynamic parameters have been estimated. In line with an associative reaction, the equilibrium 5a results to be exothermic with an unfavourable entropy change ($\Delta H° = -26.5 \pm 2.1$ kJ mol^{-1}, $\Delta S° = -74 \pm 7$ JK^{-1} mol^{-1}). This is the reason why at higher temperatures, where the entropic factor prevails, the position of equilibrium 5a is driven to the left, observing an increase of the concentration of unreacted **1**. The same signs of the thermodynamic parameters, but with much smaller values, have been calculated for the isomerization equilibrium 5b ($\Delta H° = -7.3 \pm 2$ kJ mol^{-1}, $\Delta S° = -24 \pm 8$ JK^{-1} mol^{-1}). Hence, the isomer ratio, quite close to 1 observed at the investigated temperature (see Table 2 and Fig. 7), arises from the balance of the two thermodynamic parameters having an opposite sign. In particular, it arises from the negative entropy of the **4b** formation. Indeed, the enthalpy value by itself would impose a large dominance of **4b** (with a K_2 value close to 20, instead of 1).

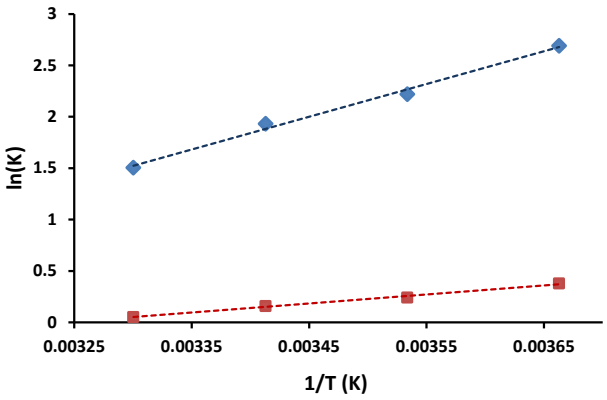


Fig. 8. Van't Hoff plots for the K_1 (blue diamonds) and K_2 (red squares) constants of Table 2.

Table 2 Values of K_1 and K_2 at different temperatures

T	***K₁***	***K₂***
273	14.8	1.45
283	9.1	1.28
293	7.0	1.16
303	4.4	1.06

First-order plots indicate that the decrease of ln[**1**] is satisfactorily linear up to at least 50% of conversion, as shown in Fig. S5. At longer times the process slows down, the effect of the reversibility becoming progressively more significant. Surprisingly, the *k* values, obtained from the fitting of the initial rates, are little affected by the concentration of the entering ligand: for instance at 263 K, the estimated *k* values are 6.0×10^{-4} s^{-1}, 6.4×10^{-4} s^{-1}, and 7.1×10^{-4} s^{-1}, with 10, 20, and 30 equivalents of MeCN, respectively. This suggests that the reaction mainly goes through a mechanism in which the rate-determining step is the opening of the triple-bridging coordination of the methyl group, to give a $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9]^-$ intermediate with a coordinatively unsaturated rhenium vertex. To account for the kinetically preferred formation of the *anti* isomer, it is worth noting that the triangular face of **1**, opposite to the μ_3-CH_3 group, is sterically more accessible, allowing an easier approach of the incoming MeCN. In the transition state, such *anti* accessibility is likely further increased by the geometrical rearrangement of the carbonyls on the apical vertex occurring upon the removal of the methyl group, before the full availability of the *syn* site.

Values of the kinetic constant for the reaction with 10 equivalents of MeCN have been determined at three different temperatures (253 K, $k = 1.42\times10^{-4}$ s^{-1}; 263 K, $k = 6.00\times10^{-4}$ s^{-1}, 273 K, $k = 1.87\times10^{-3}$ s^{-1}), allowing an estimate of the activation energy as 74(3) kJ mol^{-1} (see the Arrhenius plot in Fig. S6).

The two adducts **4** are stable in CD_2Cl_2 solution at room temperature for several hours, in the presence of a moderate excess of MeCN (10 equivalents). In neat CD_3CN, where the more polar **4b** isomer is more favoured ([**4b**]/[**4a**] = 4 at room temperature, with respect to ca. 1 in CD_2Cl_2), the stability is much lower: after 30 min the resonances of the adducts **4** are no more detectable, replaced by a multitude of hydrido signals, only partially identified. The most intense signals are attributable to the unsaturated cluster anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$ [29], formally derived from **4** by substitution of the methyl group by a hydride ~~for the methyl group~~. A $[Re_3(\mu$-

$H)_2(CO)_9(NCMe)_3]$ species, analogous to the $[Re_3(\mu\text{-}H)_2(CO)_{12}]$ anion formed from **2** in the presence of CO, has not been observed, indicating that cluster stabilization after methane elimination follows a different path.

*3.5 Reaction of **1** with $PMePh_2$: the two isomers of $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9(PMePh_2)]^-$ (**5**).* The reaction of **1** with another strong nucleophile, such as methyldiphenylphosphine ($PMePh_2$), has been investigated in THF-d_8. As in the case of CO, the reaction, using 1 equivalent of phosphine, is instantaneous and quantitative at room temperature. Two products are formed, that can be formulated as the *syn* and *anti* isomers of the addition derivative $[Re_3(\mu\text{-}CH_3)(\mu\text{-}H)_3(CO)_9(PMePh_2)]^-$ (**5**), in which the phosphine ligand is axially coordinated on the vertex of the cluster not involved in the Re-(μ-CH_3)Re interaction (Scheme 2, equation 3 with L = $PMePh_2$). The ^{1}H NMR spectrum shows two sets of three signals (ratio 3:1:2), at chemical shift values similar to those of **2** or **4** (Table 1 and Figure S7). The ^{31}P resonances are at –13.6 and –19.7 ppm (at 193 K), for **5a** and **5b** respectively, and the values of the ^{31}P-^{1}H coupling constants for the H_b resonances in both isomers (Table 1) are typical for phosphine ligands coordinated in *cis* to a bridging hydride in a rhenium cluster [30].

Based on the position and the relative intensities of the ^{1}H signals, a dynamic asymmetric coordination of the methyl group can be assumed for both isomers, similarly to what discussed in the previous paragraphs for anions **2** and **4**. A heteronuclear nOe experiment shows that selective saturation of the CH_3 hydrogens of **5b** leads to the increase of the intensity of its ^{31}P resonance, indicating that, even in this case, **5b** is the *syn* stereoisomer, in which the phosphine and methyl ligands lie on the same side of the triangle plane. Therefore, we can conclude that the kinetic isomer **5a** is the *anti* isomer.

In line with the behaviour of anions **4**, the isomer ratio **5a**/**5b** strongly varies with time and temperature. The ^{1}H spectrum, acquired at low temperature immediately after the addition of the phosphine ligand, shows that **5a** is largely dominant (**5a**/**5b** $\approx$ 26). However, on raising the

temperature to RT, the amount of **5b** strongly increases in a few minutes. Differently from what observed for the isomers **4**, at longer times the *syn* isomer **5b** becomes the only species detected in solution, which remains stable in THF at room temperature for several days.

*3.6 Behaviour of **1** in tetrahydrofuran solution.* THF is a too weak ligand to open the triple bridging methyl group. Evidence of the possible formation of a $[Re_3(\mu\text{-}H)_3(\mu\text{-}CH_3)(CO)_9(THF)]^-$ derivative (**6**) is only obtained at low temperature (193 K) and upon using THF as solvent. Under these conditions, a weak ^{1}H NMR signal is detected at –3.38 ppm, a position typical of the bridging methyl group in this class of compounds (see Table 1). However, even at such a low temperature, the amount of the adduct is low ([**6**]/[**1**] ratio = 0.12) and the signals of the hydrides in the postulated complex **6** could not be assigned with certainty (tentative δ values at -9.50 and -10.88 ppm, ratio 0.33 and 0.66, respectively) [31]. This low concentration, together with the thermal instability, hampers to establish the *syn*/*anti* configuration of **6**. However, it can be reasonably supposed, on the basis of the previous studies with MeCN and $PMePh_2$, that the species observed in these conditions (193 K) is the kinetic *anti* isomer.

At room temperature in THF, even in the absence of detectable amounts of the derivative **6**, the anion **1** is markedly unstable. Methane evolution has been observed, as indicated by GLC analysis and by the growth of the ^{1}H NMR resonance at 0.22 ppm. The disappearance of **1** followed a clean *pseudo* first-order kinetics, with $t_{1/2}$ = 74 min at 295 K (k = 1.56x10^{-4} s^{-1}) over the whole reaction course until complete consumption of **1**. The main product was a species responsible for a signal at -5.50 ppm, that can be tentatively formulated as a member of the family of unsaturated dimers $[Re_2(\mu\text{-}H)_2(CO)_6(L)_2]$ where L = THF. Complexes of this family, containing a $Re(\mu\text{-}H)_2Re$ moiety, are known for L = CO [32], bis(diphenylphosphino)methane (dppm) [33], 1,2-diazines, [34] and oxadiazole [35]. All these complexes display hydride resonances at chemical shifts lower than those usually observed for related saturated complexes containing the Re(μ-H)Re interactions [36].

The formulation of the dimer $[Re_2(\mu\text{-}H)_2(CO)_6(THF)_2]$ is supported by its reaction with one equivalent of dppm, which substitutes the labile THF ligands only once the massive THF-d_8 solvent is removed by evaporation to dryness. Indeed, upon re-dissolution in $CDCl_3$, the ^1H NMR spectrum shows the hydride resonance of the expected $[Re_2(\mu\text{-}H)_2(CO)_6(dppm)]$ product (triplet at -7.54 ppm) [33], providing indirect confirmation of the nature of the starting reactant.

Conclusions

We have shown that the reaction of **1** with CO proceeds in a stepwise manner, being the first step the irreversible conversion of CH_3 from μ_3- to μ- coordination, eventually giving the anion **2**. Low temperature NMR spectra, the isotopic perturbation experiment and the solid state structure clearly confirmed the formation of an asymetrically bridging methyl group in which only one of the three C-H bonds is involved in an agostic interaction. However, in solution, the exchange between the terminal and the agostic methyl hydrogens is so fast that it results in an apparent C_s symmetry, even at very low temperatures, affording an averaged signal for the methyl resonance. Further addition of CO caused reductive elimination of methane, without spectroscopic evidence neither of the intermediate with terminally coordinated CH_3 nor of any product of insertion of CO into the metal-methyl bond. These results confirm that the stability of a methyl group on a hydrogen-saturated metal surface increases with the number of metal atoms interacting with the methyl fragment. Hence, while the coordination on three metal centres in **1** makes the CH_3 ligand rather inert, the interaction of the μ-CH_3 in **2** with only two metal centres cannot avoid the fast decomposition of this anion. The derivative containing terminally coordinated CH_3 (if formed) could not even be observed, due to very fast methane reductive elimination.

An addition reaction occurs also using ligands different from CO, leading to the formation of *syn* and *anti* isomers, whose kinetic and thermodynamic stability varies as a function of the nucleophilicity of the ligand. In the case of the strong nucleophile $PMePh_2$ the conversion of anion

1 into the thermodynamic *syn* isomer **5b** is quantitative and this isomer is stable at room temperature for days, suggesting that the presence of a strong σ-donating ligand prevents the reductive elimination of CH_4 that preferably takes place on electron-poor metal centres. On the contrary, using weak nucleophiles such as MeCN or THF, an equilibrium mixture containing a residual amount of anion **1** is formed, whose composition varies as a function of the concentration of the entering ligand.

However, even if almost all the products proved to be less stable than the parent anion **1**, their stability is high enough to allow their complete characterization in solution and also in the solid-state for the anion **2**.

We plan to investigate the possibility of tuning the reactivity of the agostic methyl group and the relative stability of the μ-bridging vs. terminal coordination by using ligands able to assume a bridging coordination (by acting as three-electron donors) that might establish competition with the agostic coordination, possibly favouring the terminal methyl coordination.

Supporting Information

Supporting Information contains figures showing details of the ^{1}H, ^{13}C NMR spectra and tables of the ^{1}H NMR data.

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