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## Insertion of heteroallenes into the rhenium-hydride bond

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#### Abstract

Dithioformato  $[Re{\eta^2-SC(H)S}(NO)P_3]BPh_4$  (1), thioformamido  $[Re{\eta^2-RNC(H)S}(NO)P_3]BPh_4$  (2) (R = Et, *p*-tolyl), formamido  $[Re{\eta^2-PhNC(H)O}(NO)P_3]BPh_4$  (3) and formamidinato  $[Re{\eta^2-p-tolylNC(H)Np-tolyl}(NO)P_3]BPh_4$  (4) (P = PPh\_2OEt) complexes were prepared by allowing the hydride  $ReH_2(NO)P_3$  to react first with triflic acid and then with the appropriate heteroallene CS<sub>2</sub>, RNCS, PhNCO and *p*-tolylNCN*p*-tolyl. Treatment of the  $ReH_2(NO)L(PPh_3)_2$  [L = P(OEt)<sub>3</sub>, PPh(OEt)<sub>2</sub>] and  $ReH_2(NO)$ (PPh<sub>3</sub>)<sub>3</sub> hydrides first with triflic acid and then with isothiocyanate RNCS (R = Et, *p*-tolyl) gave the  $[Re{\eta^2-RNC(H)S}(NO)$ {P(OEt)<sub>3</sub>}(PPh\_3)<sub>2</sub>]BPh<sub>4</sub> (5, 6) and  $[Re(\eta^2-RNC(H)S)(NO)(PPh_3)_3]BPh_4$  (7) derivatives. Depending on the nature of the phosphite, instead, the reaction of  $ReH_2(NO)L(PPh_3)_2$  and  $ReH_2(NO)(PPh_3)_3$  hydrides first with CF<sub>3</sub>SO<sub>3</sub>H and then with isocyanate R1NCO (R1 = Ph, *p*-tolyl) gave the chelate  $[Re{\eta^2-R1NC(H)O}(NO){P(OEt)_3}(PPh_3)_2]BPh_4$  (8) and  $[Re{\eta^2-R1NC(H)O}{(NO)(PPh_3)_3]BPh_4$  (10) complexes with P(OEt)<sub>3</sub> or PPh<sub>3</sub>, while the  $\eta^1$ -coordinate  $[Re{\eta^1-RNC(H)S}(NO){PPh(OEt)_2}_2(PPh_3)_2]BPh_4$  (11) and formato  $[Re{\eta^1-OC(H)=O}(NO){PPh(OEt)_2}_2(PPh_3)_2]BPh_4$  (12) complexes, as well as the formamidinato  $[Re{\eta^2-p-tolylNC(H)Np-tolyl}(NO){P(OEt)_3}(PPh_3)_2]BPh_4$  (13) derivative were also prepared. © 2005 Elsevier B.V. All rights reserved.

Keywords: Formamido; Thioformamido; Formato; Dithioformato; Heteroallenes; Hydride; P ligands; Rhenium

### 1. Introduction

The insertion of heteroallenes such as  $CO_2$ ,  $CS_2$ , RNCO, and RNCS into the metal-hydride bond is an important chemical step in functionalizing these molecules [1–6].  $CO_2$  has drawn the most attention due to its potential usefulness as a C1 building block in constructing higher organic structures [1a,4]. However, the reaction of other heteroallenes has also been extensively studied not only as a model for  $CO_2$  but also because the isocyanate or isothiocyanate functionality is useful as a source of carbon, nitrogen, and oxygen or sulfur in one chemical step [1–3]. Thus, a number of studies on the insertion reaction of these small unsaturated mole-

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cules into the M – H bond have been reported giving formato, thioformato, formamido, thioformamido, and formamidinato derivatives bonded to the metal either in  $\eta^1$ - or  $\eta^2$ -fashion [2,3,6].

Not only does the iron triad play a prominent role among the metal centers involved in these reactions, but ruthenium complexes have also recently been reported to catalyze the hydrogenation of carbon dioxide to formic acid [4]. In contrast, few studies have been reported on the manganese triad [3b,5] and on the rhenium as a central metal [5].

We are interested in the synthesis and reactivity of transition metal hydrides [7] and have previously reported on the reactivity with heteroallenes of hydride complexes of the iron triad of the  $[MH(\eta^2-H_2)P_4]^+$  (M = Fe, Ru, Os; P = phosphite) type, which led to the synthesis of dithioformato, formamido and formamidinato derivatives [6]. Now we have extended these studies

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to include rhenium as a central metal and in this paper we report some studies on the insertion reaction of carbon disulfide, carbon dioxide, *N*-substituted isocyanate and isothiocyanate, and carbodiimide into the Re(I)-hydride bonds of rhenium phosphite derivatives.

### 2. Experimental

#### 2.1. General considerations

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under an inert atmosphere at -25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphites PPh(OEt)<sub>2</sub> and PPh<sub>2</sub>OEt were prepared by the method of Rabinowitz and Pellon [8], whereas P(OEt)<sub>3</sub> was an Aldrich product, purified by distillation under nitrogen. The heteroallenes CS<sub>2</sub>, p-tolylNCS, EtNCS, PhNCO, p-tolylNCO, and p-tolylNCNp-tolyl were Aldrich products used without any further purification. Other reagents were purchased from commercial sources (Aldrich, Fluka) in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) were obtained on Bruker AC200 or AVANCE 300 spectrometers at temperatures varying between -90 and +30 °C, unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C spectra are referred to internal tetramethylsilane, while  ${}^{31}P{}^{1}H$  chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>, with downfield shifts considered positive. The COSY, HMQC and HMBC NMR experiments were performed using their standard programs. The swan-mr software package [9] was used to treat NMR data. The conductivities of  $10^{-3}$  M solutions of the complexes in CH<sub>3</sub>NO<sub>2</sub> at 25 °C were measured with a Radiometer CDM 83 instrument. Elemental analyses were determinated in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche of the University of Padova (Italy).

#### 2.2. Synthesis of complexes

The ReH<sub>2</sub>(NO)(PPh<sub>2</sub>OEt)<sub>3</sub>, ReH<sub>2</sub>(NO)L(PPh<sub>3</sub>)<sub>2</sub> [L =  $P(OEt)_3$  and  $PPh(OEt)_2$ ] and  $ReH_2(NO)(PPh_3)_3$  hydrides were prepared following the methods previously reported [7f,10,11].

## 2.2.1. $[Re \{\eta^2 - SC(H)S\}(NO)(PPh_2OEt)_3]BPh_4(1)$

An equimolar amount of  $CF_3SO_3H$  (0.11 mmol, 10 µL) was added to a solution of  $ReH_2(NO)(PPh_2-OEt)_3$  (100 mg, 0.11 mmol) in 10 mL of  $CH_2Cl_2$  cooled to -196 °C. The reaction mixture was brought to -30 °C, stirred for about 1 h and then an excess of CS<sub>2</sub> (0.38 mmol, 23 μL) was added. The solution was allowed to reach the room temperature, stirred for about 6 h and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol containing an excess of NaBPh<sub>4</sub> (0.22 mmol, 75 mg) in 1 mL of ethanol. A yellow-orange solid slowly separated out which was collected by filtration and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; Yield: ≥65%. Calc. for C<sub>67</sub>H<sub>66</sub>BNO<sub>4</sub>P<sub>3</sub>ReS<sub>2</sub> (1303.31): C, 61.75; H, 5.10; N, 1.07; S, 4.92. Found: C, 61.58; H, 5.03; N, 1.15; S, 4.75%. Λ<sub>M</sub> = 51.4 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>.

## 2.2.2. $[Re \{\eta^2 - RNC(H)S\}(NO)(PPh_2OEt)_3]BPh_4$ (2) [R = Et (a), p-tolyl (b)]

An equimolar amount of CF<sub>3</sub>SO<sub>3</sub>H (0.11 mmol, 10 µL) was added to a solution of ReH<sub>2</sub>(NO)(PPh<sub>2</sub>-OEt)<sub>3</sub> (100 mg, 0.11 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> cooled to -196 °C. The reaction mixture was brought to -30 °C, stirred for about 1 h and then an excess of the appropriate isothiocyanate RNCS (1.7 mmol) was added. The solution was allowed to reach the room temperature and then stirred for about 7 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol containing an excess of NaBPh<sub>4</sub> (0.22 mmol, 75 mg) in 1 mL of ethanol. A yellow solid slowly separated out which was collected by filtration and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol. A typical crystallization involved the slow cooling to -25 °C of a solution of the complex prepared by adding 5 mL of ethanol and enough CH<sub>2</sub>Cl<sub>2</sub> to obtain a saturated solution at room temperature; Yield:  $\geq 65\%$ .

**2a:** Calc. for C<sub>69</sub>H<sub>71</sub>BN<sub>2</sub>O<sub>4</sub>P<sub>3</sub>ReS (1314.32): C, 63.06; H, 5.44; N, 2.13; S, 2.44. Found: C, 62.85; H, 5.60; N, 2.15; S, 2.31%.  $\Lambda_{\rm M} = 50.8 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$ .

**2b:** Calc. for  $C_{74}H_{73}BN_2O_4P_3ReS$  (1376.39): C, 64.58; H, 5.35; N, 2.04; S, 2.33. Found: C, 64.39; H, 5.42; N, 2.10; S, 2.16%.  $\Lambda_M = 54.6 \ \Omega^{-1} \ mol^{-1} \ cm^2$ .

## 2.2.3. $[Re \{\eta^2 - PhNC(H)O\}(NO)(PPh_2OEt)_3]BPh_4$ (3)

This complex has been prepared following the method used for the related isothiocyanate complexes **2**; Yield:  $\ge 45\%$ . Calc. for C<sub>73</sub>H<sub>71</sub>BN<sub>2</sub>O<sub>5</sub>P<sub>3</sub>Re (1346.31): C, 65.13; H, 5.32; N, 2.08. Found: C, 64.90; H, 5.40; N, 2.07%.  $\Lambda_{\rm M} = 56.5 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$ .

## 2.2.4. [ $Re\{\eta^2$ -p-tolyl-NC(H)N-p-tolyl $\}(NO)$ -( $PPh_2OEt$ )<sub>3</sub>] $BPh_4$ (4)

In a 25-mL three-necked round-bottomed flask, 150 mg (0.17 mmol) of ReH<sub>2</sub>(NO)(PPh<sub>2</sub>OEt)<sub>3</sub>, 250 mg (1.12 mmol) of 1,3-di-*p*-tolylcarbodiimide and 10 mL of CH<sub>2</sub>Cl<sub>2</sub> were placed. The flask was cooled to -196 °C and triflic acid (0.17 mmol, 15 µL) was added. The reaction mixture was brought to 0 °C and stirred for 12 h. The solvent was removed under reduced pressure to give

an oil which was treated with ethanol containing an excess of NaBPh<sub>4</sub> (0.24 mmol, 82 mg). A yellow-orange solid slowly separated out which was collected by filtration and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; Yield:  $\geq$  65%. Calc. for C<sub>81</sub>H<sub>80</sub>BN<sub>3</sub>O<sub>4</sub>P<sub>3</sub>Re (1449.47): C, 67.12; H, 5.56; N, 2.90. Found: C, 67.39; H, 5.64; N, 2.84%.  $\Lambda_{\rm M} = 53.3 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$ .

2.2.5.  $[Re \{\eta^2 - RNC(H)S\}(NO)L(PPh_3)_2]BPh_4$  (5, 6)  $[L = P(OEt)_3$  (5),  $PPh(OEt)_2$  (6); R = Et (a), p-tolyl (b)]

An equimolar amount of  $CF_3SO_3H$  (0.1 mmol, 9 µL) was added to a solution of the appropriate hydride ReH<sub>2</sub>(NO)L(PPh<sub>3</sub>)<sub>2</sub> (0.1 mmol) in 7 mL of CH<sub>2</sub>Cl<sub>2</sub> cooled to -196 °C. The reaction mixture was brought to room temperature, stirred for 30 min and then cooled again to -196 °C. An excess of the appropriate isothiocyanate RNCS (0.5 mmol) was added and the solution, brought to room temperature, stirred for about 4 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol containing an excess of NaBPh<sub>4</sub> (0.32 mmol, 110 mg). A yellow solid slowly separated out which was collected by filtration and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; Yield:  $\geq 65\%$ .

**5a:** Calc. for C<sub>69</sub>H<sub>71</sub>BN<sub>2</sub>O<sub>4</sub>P<sub>3</sub>ReS (1314.32): C, 63.06; H, 5.44; N, 2.13; S, 2.44. Found: C, 62.88; H, 5.52; N, 2.18; S, 2.30%.  $\Lambda_{\rm M}$  = 53.7  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>.

**5b:** Calc. for C<sub>74</sub>H<sub>73</sub>BN<sub>2</sub>O<sub>4</sub>P<sub>3</sub>ReS (1376.39): C, 64.58; H, 5.35; N, 2.04; S, 2.33. Found: C, 64.40; H, 5.46; N, 2.12; S, 2.27%.  $\Lambda_{\rm M}$  = 55.1  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>.

**6a:** Calc. for C<sub>73</sub>H<sub>71</sub>BN<sub>2</sub>O<sub>3</sub>P<sub>3</sub>ReS (1346.37): C, 65.12; H, 5.32; N, 2.08; S, 2.38. Found: C, 65.37; H, 5.45; N, 1.97; S, 2.28%.  $\Lambda_{\rm M}$  = 54.3 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>.

**6b:** Calc. for C<sub>78</sub>H<sub>73</sub>BN<sub>2</sub>O<sub>3</sub>P<sub>3</sub>ReS (1408.44): C, 66.52; H, 5.22; N, 1.99; S, 2.28. Found: C, 66.34; H, 5.31; N, 2.08; S, 2.21%.  $\Lambda_{\rm M}$  = 52.6  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>.

## 2.2.6. $[Re \{\eta^2 - p - tolyl - NC(H)S\}(NO)(PPh_3)_3]BPh_4(7)$

This complex was prepared exactly like the related thioformamido complexes **5**, **6** using ReH<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>3</sub> as a precursor; Yield:  $\geq 70\%$ . Calc. for C<sub>86</sub>H<sub>73</sub>BN<sub>2</sub>-OP<sub>3</sub>ReS (1472.53): C, 70.15; H, 5.00; N, 1.90; S, 2.18. Found: C, 70.26; H, 5.11; N, 1.79; S, 2.06%.  $\Lambda_{\rm M} = 55.3 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$ .

## 2.2.7. $[Re \{\eta^2 - RNC(H)O\}(NO) \{P(OEt)_3\}(PPh_3)_2]$ -BPh<sub>4</sub> (8) [R = p-tolyl (b), Ph (c)] and $[Re \{\eta^2 - p$ -tolyl-NC(H)O}(NO)(PPh\_3)\_3]BPh\_4 (10)

These complexes were prepared following the method used for the related thioformamido complexes 5, 6 using the appropriate RNCO as a reagent in a 5:1 ratio; Yield: between 55% (8b, 8c) and 60% (10).

**8b:** Calc. for  $C_{74}H_{73}BN_2O_5P_3Re$  (1360.33): C, 65.34; H, 5.41; N, 2.06. Found: C, 65.08; H, 5.52; N, 2.12%.  $\Lambda_M = 55.0 \ \Omega^{-1} \ mol^{-1} \ cm^2$ . 8c: Calc. for C<sub>73</sub>H<sub>71</sub>BN<sub>2</sub>O<sub>5</sub>P<sub>3</sub>Re (1346.31): C, 65.13; H, 5.32; N, 2.08. Found: C, 64.87; H, 5.41; N, 2.01%.  $\Lambda_{\rm M} = 51.8 \,\Omega^{-1} \, {\rm mol}^{-1} \, {\rm cm}^2.$ 

**10:** Calc. for C<sub>86</sub>H<sub>73</sub>BN<sub>2</sub>O<sub>2</sub>P<sub>3</sub>Re (1456.47): C, 70.92; H, 5.05; N, 1.92. Found: C, 71.13; H, 5.16; N, 2.04%.  $\Lambda_{\rm M} = 53.4 \,\Omega^{-1} \, {\rm mol}^{-1} \, {\rm cm}^2$ .

## 2.2.8. $[Re \{\eta^{1}-RNC(H)O\}(NO) \{PPh(OEt)_{2}\}_{2}$ - $(PPh_{3})_{2}]BPh_{4}$ (9) [R = p-tolyl (b), Ph (c)]

An equimolar amount of CF<sub>3</sub>SO<sub>3</sub>H (0.1 mmol, 9 µL) was added to a solution of ReH<sub>2</sub>(NO)[P-Ph(OEt)<sub>2</sub>](PPh<sub>3</sub>)<sub>2</sub> (0.1 mmol, 94 mg) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> cooled to -196 °C. The reaction mixture was brought to room temperature, stirred for 30 min and then cooled again to -196 °C. An excess of the appropriate isocyanate RNCO (0.5 mmol) was added and the resulting solution stirred for about 4 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol containing an excess of NaBPh<sub>4</sub> (0.32 mmol, 110 mg). A yellow solid slowly separated out which was collected by filtration and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; Yield:  $\geq 40\%$ .

**9b:** Calc. for  $C_{88}H_{88}BN_2O_6P_4Re$  (1590.58): C, 66.45; H, 5.58; N, 1.76. Found: C, 66.23; H, 5.66; N, 1.89%.  $\Lambda_M = 54.7 \ \Omega^{-1} \ mol^{-1} \ cm^2$ .

**9c:** Calc. for C<sub>87</sub>H<sub>86</sub>BN<sub>2</sub>O<sub>6</sub>P<sub>4</sub>Re (1576.55): C, 66.28; H, 5.50; N, 1.78. Found: C, 66.04; H, 5.64; N, 1.90%.  $\Lambda_{\rm M}$  = 55.2  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>.

2.2.9.  $[Re \{\eta^1 - SC(H)S\}(NO) \{PPh(OEt)_2\}_2(PPh_3)_2] - BPh_4$  (11)

This compound was prepared following the method used for the related formamido complexes **9b** and **9c** using CS<sub>2</sub> as a reagent with a reaction time of 6 h; Yield:  $\geq 45\%$ . Calc. for C<sub>81</sub>H<sub>81</sub>BNO<sub>5</sub>P<sub>4</sub>ReS<sub>2</sub> (1533.56): C, 63.44; H, 5.32; N, 0.91; S, 4.18. Found: C, 63.61; H, 5.43; N, 1.02; S, 4.05\%.  $\Lambda_{\rm M} = 51.8 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$ .

## 2.2.10. $[Re \{\eta^1 - OC(H)O\}(NO) \{PPh(OEt)_2\}_2 - (PPh_3)_2]BPh_4$ (12)

Triflic acid (0.1 mmol, 9 µL) was added to a solution of ReH<sub>2</sub>(NO)[PPh(OEt)<sub>2</sub>](PPh<sub>3</sub>)<sub>2</sub> (0.1 mmol, 94 mg) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> cooled to -196 °C. The reaction mixture was brought to room temperature, stirred for 30 min and then allowed to stand under CO<sub>2</sub> (1 atm) for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL) containing an excess of NaBPh<sub>4</sub> (0.3 mmol, 103 mg). By cooling of the resulting solution to -25 °C, a yellow solid slowly separated out which was collected by filtration and crystallized from CH<sub>2</sub>Cl<sub>2</sub> and ethanol; Yield:  $\ge 40\%$ . Calc. for C<sub>81</sub>H<sub>81</sub>BNO<sub>7</sub>P<sub>4</sub>Re (1501.44): C, 64.80; H, 5.44; N, 0.93. Found: C, 64.98; H, 5.61; N, 0.88%.  $\Lambda_{\rm M} = 52.6 \,\Omega^{-1} \,{\rm mol}^{-1} \,{\rm cm}^2$ .

## 2.2.11. $[Re \{\eta^2 - p - tolyl - NC(H)N - p - tolyl\}(NO) - \{P(OEt)_3\}(PPh_3)_2]BPh_4$ (13)

An equimolar amount of triflic acid (0.1 mmol, 9  $\mu$ L) was added to a solution of ReH<sub>2</sub>(NO)[P(OEt)<sub>3</sub>](PPh<sub>3</sub>)<sub>2</sub> (0.1 mmol, 91 mg) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> cooled to -196 °C. The reaction mixture was brought to room temperature, stirred for 30 min and then cooled again to -196 °C. An excess of p-tolyl-NCN-p-tolyl (1 mmol, 222 mg) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added and the solution, brought to room temperature, stirred for about 5 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol (2 mL) containing an excess of NaBPh<sub>4</sub> (0.2 mmol, 68 mg). A yellow solid slowly separated out which was collected by filtration and crystallized from CH2Cl2 and ethanol; Yield:  $\geq 65\%$ . Calc. for  $C_{81}H_{80}BN_3O_4P_3Re$  (1449.47): C, 67.12; H, 5.56; N, 2.90. Found: C, 66.95; H, 5.65; N, 2.85%.  $\Lambda_{\rm M} = 54.4 \ \Omega^{-1} \ {\rm mol}^{-1} \ {\rm cm}^2$ .

#### 3. Results and discussion

The synthesis of dithioformato (1), thioformamido (2), formamido (3), and formamidinato (4) complexes of rhenium was achieved by reacting the  $\text{ReH}_2(\text{NO})(\text{P-Ph}_2\text{OEt})_3$  hydride first with triflic acid and then with the appropriate heteroallene, as shown in Scheme 1.

The reaction of  $ReH_2(NO)(PPh_2OEt)_3$  with  $CF_3SO_3H$  proceeds [7f] with the evolution of  $H_2$  and formation of the triflate  $ReH(\kappa^1-OSO_2CF_3)(NO)P_3$ 

complexes, which react with the heteroallenes to give the insertion products 1–4 which were isolated as orange or yellow solids and characterized. A geometry in solution of the type of Scheme 1 was also established with the ligand formed upon insertion resulting in  $\eta^2$ -coordinated to the metal center.

We also reacted the ReH<sub>2</sub>(NO)P<sub>3</sub> dihydride with heteroallenes both at room temperature and at reflux, but no insertion reaction was observed and the starting complexes were recovered unchanged after several hours of reaction. The insertion of X=C=Y into rhenium complexes, therefore, needs the presence of an open coordination site to occur and the presence of the labile  $\kappa^1$ -triffate ligand in ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)P<sub>3</sub> allows the probable initial coordination of the heteroallene prior to insertion into the Re–H bond to give the 1–4 derivatives.

Insertion reactions of heteroallene into the M–H bond of rhenium complexes have few precedents [5] and the use of dihydride complexes  $\text{ReH}_2(\text{NO})\text{P}_3$  as a precursor allows, after protonation, the facile syntheses of new dithioformato, thioformamido, formamido and formamidinato derivatives.

All the complexes 1–4 were isolated as yellow to orange solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [12]. Analytical and spectroscopic (IR and <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR) data (Table 1) support the proposed formulation and a geometry in solution was also established. Attempts were also made to obtain structural information in the



Scheme 1.  $P = PPh_2OEt$ ; R = Et(a), *p*-tolyl (b); R1 = p-tolyl.

Complex	$IR^{a} (cm^{-1})$	Assgnt	<sup>1</sup> H NMR <sup>b,c</sup>		Spin system	${}^{31}P{}^{1}H} NMR^{b,d}$	$^{13}C{^{1}H} NMR^{b,e}$	
			δ ( <i>J</i> /Hz)	Assgnt		$\delta$ (J/Hz)	δ (J/Hz)	Assgnt
[Re{η <sup>2</sup> -SC(H)S}(NO)(PPh <sub>2</sub> OEt) <sub>3</sub> ]BPh <sub>4</sub> (1)	1729 s	ν(NO)	AB <sub>2</sub> X spin system (X = <sup>1</sup> H) $\delta_X$ 11.15 $J_{AX}$ = 10.3 $J_{BX}$ = 8.65 3.60 m 3.45 qnt 1.07 t 0.84 t	СН СН <sub>2</sub> СН <sub>3</sub>	AB <sub>2</sub>	$\delta_{A} \ 112.5$ $\delta_{B} \ 102.6$ $J_{AB} = 23.5$	AB <sub>2</sub> X spin system (X = ${}^{13}$ C) $\delta_X$ 234.6 $J_{AX}$ = 7 $J_{BX}$ = 0.6 65.7 m 15.8 m	CH CH <sub>2</sub> CH <sub>3</sub>
$[Re{\eta^2-EtNC(H)S}(NO)(PPh_2OEt)_3]BPh_4 (2a)$	1722 s	v(NO)	AB <sub>2</sub> XY <sub>2</sub> spin system (X = <sup>1</sup> H) (Y = <sup>1</sup> H, CH <sub>2</sub> ) $\delta_X$ 8.63	СН	AB <sub>2</sub>	$\delta_{A} \ 112.8$ $\delta_{B} \ 99.2$ $J_{AB} = 17.8$	176.2 dt 53.1 s 12.5 s	CH CH <sub>2</sub> EtN CH <sub>3</sub> EtN
			$J_{AX} = 10.4$ $J_{BX} = 2.9$ $J_{XY} = 1.5$ 2.97 g	CH2EtN	AB <sub>2</sub>	$\delta_{A} 111.1$ $\delta_{B} 107.8$ $J_{AB} = 21.0$	182.4 t 48.9 s 11.3 s	CH CH <sub>2</sub> EtN CH <sub>3</sub> EtN
			0.66 t	CH <sub>3</sub> EtN			65.2 m 15.8 m	CH₂phos CH₃phos
			AB <sub>2</sub> XY <sub>2</sub> spin system (X = <sup>1</sup> H) (Y = <sup>1</sup> H, CH <sub>2</sub> ) $\delta_X$ 8.27 $J_{AX}$ = 4.3 $J_{BX}$ = 3.8 $J_{XY}$ = 1.1 1.65 q 0.15 t 3.66–3.15 m 1.06 t 1.03 t	CH CH2EtN CH3EtN CH2phos CH3phos			13.6 m	
$[Re{\eta^2-p-tolylNC(H)S}(NO)(PPh_2OEt)_3]BPh_4 (2b)$	1710 s	v(NO)	AB <sub>2</sub> X spin system (X = <sup>1</sup> H) $\delta_X$ 9.04 $J_{AX} = 5.34$	СН	AB <sub>2</sub>	$\delta_{A} 113.8$ $\delta_{B} 99.7$ $J_{AB} = 19.0$ $\delta_{AB} = 104.5$	AB <sub>2</sub> X spin system (X = ${}^{13}$ C) $\delta_X$ 185.9 $J_{AX}$ = 1.1 $L_{YZ}$ = 6.1	СН
			2.20 s	CH <sub>3</sub> <i>p</i> -tol	$AD_2$	$\delta_{\rm B} \ 101.0$ $J_{\rm AB} = 21.4$	21.3 s	CH <sub>3</sub> <i>p</i> -tol
			AB <sub>2</sub> X spin system (X = <sup>1</sup> H) $\delta_X$ 8.82 $J_{AX} = 10.3$ $J_{BX} = 3.20$	СН			AB <sub>2</sub> X spin system (X = $^{13}$ C) $\delta_X$ 175.4 $J_{AX}$ = 3.9 $J_{BX}$ = 4.5 (continued on	CH CH <sub>3</sub> p-tol CH on next page)

# Table 1 IR and NMR spectroscopic data for rhenium complexes

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Table 1 (continued)								
Complex	$IR^{a} (cm^{-1})$	Assgnt	<sup>1</sup> H NMR <sup>b,c</sup>		Spin system	${}^{31}P{}^{1}H} NMR^{b,d}$	$^{13}C{^{1}H} NMR^{b,e}$	
			$\delta$ (J/Hz)	Assgnt		$\delta$ (J/Hz)	$\delta$ (J/Hz)	Assgnt
			2.37 s 3.59 m 3.31 qnt	CH <sub>3</sub> <i>p</i> -tol CH <sub>2</sub>			21.0 s 65.6 d 65.4 t	CH <sub>3</sub> <i>p</i> -tol CH <sub>2</sub>
			0.99 t 0.94 t 0.85 t	CH <sub>3</sub> phos			15.8 m	CH <sub>3</sub> phos
$[Re{\eta^2-PhNC(H)O}(NO)(PPh_2OEt)_3]BPh_4 (3)$	1722 s	v(NO)	AB <sub>2</sub> X spin system (X = ${}^{1}$ H) $\delta_{X}$ 8.23	СН	AB <sub>2</sub>	$\delta_{A} \ 117.7 \\ \delta_{B} \ 108.0 \\ J_{AB} = 17.2$	165.7 t 65.6 d 65.0 t	CH CH <sub>2</sub>
			$J_{AX} = 4$				15.6 t	$CH_3$
			3.60–3.15 m	$CH_2$	15 <sup>1</sup> 2	15.5 u		
			0.75 t 0.57 t	CH <sub>3</sub>				
$[Re\{\eta^2\text{-}p\text{-}tolylN\text{-}C(H)\text{-}Np\text{-}tolyl\}(NO)(PPh_2OEt)_3]BPh_4 \text{ (4)}$	1723 s	v(NO)	7.70 m 3.55 gnt	CH CH <sub>2</sub>	AB <sub>2</sub>	$\delta_A 112.5$ $\delta_B 107.2$	156.8 t 65.6 m	CH CH <sub>2</sub>
			3.28 m			$J_{AB} = 21.8$	20.8 s	CH <sub>3</sub> p-tol
			2.25 s CH <sub>3</sub> p-tol 2.23 s			20.4 s 15.9 m	CH <sub>3</sub> phos	
			1.03 t 0.97 t	CH <sub>3</sub> phos				
$[Re(\eta^2-EtNC(H)S)(NO){P(OEt)_3}(PPh_3)_2]BPh_4 (\textbf{5a})$	1684 s	v(NO)	2.01 q 0.40 t	CH <sub>2</sub> EtN CH <sub>3</sub> EtN	$AB_2$	$\begin{array}{c} \delta_{\rm A} \ 97.9 \\ \delta_{\rm B} \ 16.2 \end{array}$		
			1.65 a	CH E+N		$J_{AB} = 18.0$		
			0.63 t	CH <sub>2</sub> EtN CH <sub>3</sub> EtN	AB <sub>2</sub>	δ <sub>A</sub> 98.4 δ <sub>B</sub> 15.6		
			3.60 m	CH <sub>2</sub> phos		$J_{AB} = 18.0$		
			1.11 t 1.07 t	CH <sub>3</sub> phos				
$[Re(\eta^2-p-tolylNC(H)S)(NO)\{P(OEt)_3\}(PPh_3)_2]BPh_4 \ \textbf{(5b)}$	1707 s	v(NO)	6.90 m	CH	AB <sub>2</sub>	$\delta_A$ 97.95	186.5 s, br	СН
			3.63 m 2.29 s	CH <sub>2</sub> CH <sub>3</sub> <i>p</i> -tol		$o_{\rm B} = 10.5$ $J_{\rm AB} = 18$	184.1 s, br 64.3 m	CH <sub>2</sub>
			2.19 s	Jer Jr		· Ab	25.5 s	CH <sub>3</sub> p-tol
			1.13 t	CH <sub>3</sub> phos	$AB_2$	$\delta_{\rm A} 97.95$	20.9 s	CU mbaa
			1.10 t			$J_{AB} = 18$	15.80 s	C113pilos
$[Re(\eta^2-EtNC(H)S)(NO){PPh(OEt)_2}(PPh_3)_2]BPh_4 (6a)$	1695 s	v(NO)	6.66 m	СН	AB <sub>2</sub>	$\delta_A$ 125.4 $\delta_B$ 15.2	36.0 s 13.1 s	CH <sub>2</sub> EtN CH <sub>3</sub> EtN
			2.06 q	CH <sub>2</sub> EtN		$J_{AB} = 13$		-
			0.65 t	CH <sub>3</sub> EtN	A Ba	δ. 125.1	35.7 s	CH <sub>2</sub> EtN
			1.71 q	CH <sub>2</sub> EtN	<b>ΛD</b> <sub>2</sub>	$\delta_{\rm B}$ 15.8	12.0 5	CII3EUN
			0.41 t	CH <sub>3</sub> EtN		$J_{AB} = 13$	186.4 s, br	CH

			3.71 m 1.07 t 1.06 t	CH <sub>2</sub> phos CH <sub>3</sub> phos			184.8 s, br 64.9 s, br 64.7 s, br 15.8 s 15.3 s	CH <sub>2</sub> phos CH <sub>3</sub> phos
$[Re(\eta^2-p\text{-toly}]N \cdots C(H) \cdots S)(NO) \{PPh(OEt)_2\}(PPh_3)_2]BPh_4 \ \textbf{(6b)}$	1699 s	v(NO)	6.68 m 3.73 m 2.35 s 2.23 s 1.06 t	CH CH <sub>2</sub> CH <sub>3</sub> p-tol CH <sub>3</sub> phos	AB <sub>2</sub> AB <sub>2</sub>	$\delta_{A} 126.0$ $\delta_{B} 15.4$ $J_{AB} = 13$ $\delta_{A} 125.0$	185.6 s, br 183.6 s, br 64.8 m 21.1 s 20.9 s	CH CH <sub>2</sub> CH <sub>3</sub> p-tol
			1.05 t	51	2	$\delta_{\rm B} 15.7$ $J_{\rm AB} = 13$	15.9 s 15.7 s	CH <sub>3</sub> phos
$[Re(\eta^2-p-tolylNC(H)S)(NO)(PPh_3)_3]BPh_4 (7)$	1694 s	v(NO)	2.39 s 2.25 s	CH <sub>3</sub>	A <sub>2</sub> B	$\delta_{A} 3.90$ $\delta_{B} 0.19$ $J_{AB} = 9$	187.8 s, br 185.2 s, br 21.1 s 21.6 s	CH CH <sub>3</sub>
					A <sub>2</sub> B	$\delta_{A} 2.95$ $\delta_{B} 0.74$ $J_{AB} = 9$	21.0 5	
$[Re{\eta^2-p-tolylN - C(H) - O}(NO){P(OEt)_3}(PPh_3)_2]BPh_4 (\textbf{8b})$	1710 s	v(NO)	6.85 m 6.79 m 3.65 m	CH CH <sub>2</sub> CH n tol	AB <sub>2</sub>	$\delta_{A} 98.6$ $\delta_{B} 17.0$ $J_{AB} = 17$	163.3 m, br 161.9 m, br 64.3 d	CH CH <sub>2</sub>
			2.29 s 2.21 s 1.04 t	CH <sub>3</sub> p-tor	AB <sub>2</sub>	$\delta_{A} 97.8$ $\delta_{B} 16.5$ $J_{AB} = 21$	20.8 s, br 15.8 s 15.7 s	CH <sub>3</sub> <i>p</i> -tol CH <sub>3</sub> phos
$[Re{\eta^2-PhN-C(H)-O}(NO){P(OEt)_3}(PPh_3)_2]BPh_4 (8c)$	1709 s	v(NO)	6.39 m 3.64 m 1.16 t 1.01 t	CH CH <sub>2</sub> CH <sub>3</sub>	AB <sub>2</sub>	$\delta_{A} 98.3$ $\delta_{B} 16.7$ $J_{AB} = 18$		
					AB <sub>2</sub>	$\delta_{A} 97.8$ $\delta_{B} 17.2$ $J_{AB} = 18$		
$[Re{\eta^1-p-tolylNC(H)=O}(NO){PPh(OEt)_2}_2(PPh_3)_2]BPh_4 (9b)$	1701 s 1664 m	v(NO) v(CO)	6.69 m 3.10 m 2.87 m 2.29 s 0.62 t	CH CH <sub>2</sub> CH <sub>3</sub> <i>p</i> -tol CH <sub>3</sub> phos	A <sub>2</sub> B <sub>2</sub>	$\delta_{A} 131.8$ $\delta_{B} 5.19$ $J_{AB} = 22$		
$[Re{\eta^{1}-PhNC(H)=O}(NO){PPh(OEt)_{2}}_{2}(PPh_{3})_{2}]BPh_{4} (9c)$	1702s 1660 m	v(NO) v(CO)	6.67 m 3.10 m 2.87 m 0.62 t	CH CH <sub>2</sub> CH <sub>3</sub>	$A_2B_2$	$\delta_{A} 131.8$ $\delta_{B} 5.19$ $J_{AB} = 22$	161.2 m, br 63.5 s, br 15.3 s, br	CH CH <sub>2</sub> CH <sub>3</sub>
$[Re{\eta^2-p-tolylNC(H)O}(NO)(PPh_3)_3]BPh_4 (10)$	1699 s	v(NO)	2.39 s 2.22 s	CH <sub>3</sub>	A <sub>2</sub> B	$\delta_{A} 6.79 \\ \delta_{B} 4.12 \\ J_{AB} = 6.5$	(continued)	on next page)
							(commueu (	m nesi page)

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Complex	$IR^{a} (cm^{-1})$	Assgnt	<sup>1</sup> H NMR <sup>b,c</sup>		Spin system	$^{31}P\{^{1}H\} NMR^{b,d}$	$^{13}C{^{1}H} NMR^{b,e}$	
			δ ( <i>J</i> /Hz)	Assgnt		$\delta$ (J/Hz)	$\delta$ (J/Hz)	Assgnt
					A <sub>2</sub> B	$\delta_{A} 6.09$ $\delta_{B} 3.27$ $J_{AB} = 7.3$		
$[Re{\eta^{1}-SC(H)=S}(NO){PPh(OEt)_{2}}_{2}(PPh_{3})_{2}]BPh_{4} (11)$	1709 s	v(NO)	6.72 m 3.12 m 2.89 m 0.64 t	CH CH <sub>2</sub> CH <sub>3</sub>	$A_2B_2$	$\delta_{A} 131.8$ $\delta_{B} 5.21$ $J_{AB} = 22$		
$[Re{\eta^{1}-OC(H)=O}(NO){PPh(OEt)_{2}}_{2}(PPh_{3})_{2}]BPh_{4} (12)$	1706 s 1662 m	v(NO) v(CO)	6.73 m 3.64 m 0.64 t	CH CH <sub>2</sub> CH <sub>3</sub>	$A_2B_2$	$\delta_{A} 131.8$ $\delta_{B} 5.21$ $J_{AB} = 22$	176.8 s, br 65.4 d 15.9 d	$\begin{array}{c} \mathrm{CH} \\ \mathrm{CH}_2 \\ \mathrm{CH}_3 \end{array}$
[Re(η <sup>2</sup> - <i>p</i> -tolylNC(H)N <i>p</i> -tolyl)(NO){P(OEt) <sub>3</sub> }(PPh <sub>3</sub> ) <sub>2</sub> ]BPh <sub>4</sub> ( <b>13</b> )	1700 s	v(NO)	AB <sub>2</sub> X spin system (X = <sup>1</sup> H) $\delta_X$ 6.59 $J_{AX} = 24$ $J_{PX} = 8$	СН	AB <sub>2</sub>	$\delta_{A} 105.3$ $\delta_{B} 12.0$ $J_{AB} = 18$		
			3.96 m 3.68 m 3.49 m	CH <sub>2</sub>	AB <sub>2</sub>	$\delta_{A} \ 100.3$ $\delta_{B} \ 12.7$ $J_{AB} = 19.5$		
			2.33 s 2.22 s	CH <sub>3</sub> <i>p</i> -tol				
			1.12 t 1.01 t	CH <sub>3</sub> phos				

Table 1 (continued)

<sup>a</sup> In KBr pellets.
<sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 25 °C.
<sup>c</sup> Phenyl proton resonances omitted.
<sup>d</sup> Positive shift downfield from 65% H<sub>3</sub>PO<sub>4</sub>.
<sup>e</sup> Phenyl carbon resonances omitted.

solid state for the complexes, but the poor quality of the obtained crystals prevented any X-ray determination.

The <sup>1</sup>H NMR spectrum of the thioformato Re{ $\eta^2$ -S - C(H) - S (NO)(PPh<sub>2</sub>OEt)<sub>3</sub>]BPh<sub>4</sub> (1) complex shows a multiplet at 11.15 ppm attributed to the CH proton [2,3,5] of the thioformato ligand. The multiplicity of the signal is due to the coupling with the phosphorus nuclei of the phosphine and the related NMR parameters (Table 1) can be obtained by simulation of the spectra using an AB<sub>2</sub>X (X = <sup>1</sup>H) model. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra support the presence of the SC(H)S ligand showing a AB<sub>2</sub>X (X =  $^{13}$ C) multiplet centered at 234.6 ppm of the thioformato carbon atom which, in the HMQC experiments, correlates with the CH proton signal at 11.15 ppm of the SC(H)S ligand. In the temperature range between +20 and -80 °C, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra appear as an AB<sub>2</sub> multiplet, in agreement with the presence of two phosphites magnetically equivalent and different from the third. Furthermore, the <sup>1</sup>H NMR spectra of **1** show, beside the phenyl and methyl proton signals, also a quintet at 3.45 and a multiplet at 3.60 ppm attributed to the methylene protons of the PPh<sub>2</sub>OEt ligands. The presence of a multiplet [13], beside the quintet, suggests that two of the three phosphites are in a mutually trans position. Finally, the IR spectrum shows one strong band at  $1729 \text{ cm}^{-1}$  attributed to v(NO) of the nitrosyl ligand. On the basis of these data, a geometry of type I (Scheme 1) can reasonably be proposed for the dithioformato complex 1.

The <sup>1</sup>H NMR spectra of both the thioformamido  $[Re{\eta^2-RN-C(H)-S}(NO)P_3]BPh_4$  (2a and 2b) complexes show two CH multiplets [2,3,5] at 8.63, 8.27 (2a) and at 9.04, 8.82 (2b) ppm and two signals for the substituent R of the RNC(H)S ligand. The COSY experiment allowed the easy attribution of the signals reported in Table 1. These results seem to suggest the presence of two isomers of the types shown in Scheme 1, with the NO ligand in a mutually *trans* position with the sulfur atom of RNC(H)S in one case, and in cis in the other. This is confirmed by the <sup>31</sup>P NMR spectra, which show two AB<sub>2</sub> multiplets, and by the <sup>13</sup>C spectra whose CH carbon resonances appear as two wellresolved multiplets at 182–176 (2a) and 185–175 (2b) ppm. In the spectra, two sets of signals for the substituents R of the RNC(H)S ligands are also observed, while the HMQC experiments show the correlation between the two CH proton signals between 8.26 and 9.02 ppm with the two multiplets in the <sup>13</sup>C spectra at 182-185 ppm of the CH carbon resonance of the thioformamido ligand. On the basis of these data, the geometry of Scheme 1 for the two isomers of complexes 2 can reasonably be proposed.

Surprisingly, only one isomer has been observed for the formamido  $[Re{\eta^2-PhN \dots C(H) \dots O}(NO)P_3]BPh_4$ (3) complex, whose <sup>1</sup>H NMR spectra show only one multiplet for the CH resonance at 8.23 ppm. The <sup>13</sup>C spectra confirm the presence of the formamido ligand showing the CH carbon resonance as a multiplet at 165.7 ppm. In the HMQC experiment, this signal correlates with the proton multiplet at 8.23 ppm, in agreement with the proposed attributions. In the temperature range between +20 and -80 °C, the  ${}^{31}P{}^{1}H$  NMR spectra of the formamido complex 3 appear as a AB<sub>2</sub> multiplet, suggesting the presence of two phosphines magnetically equivalent and different from the third. These data, however, do not allow to unambiguously assign a geometry for the complex, i.e., do not allow to distinguish between a geometry with the NO in the *trans* or in the *cis* position with respect to the N atom of the  $\eta^2$ -RN--C(H)--O ligand. However, the IR spectra show the v(NO) at the same values  $(1722 \text{ cm}^{-1})$  of the formamidinato complex 4 (see below) which contains a similar group trans to the NO and, therefore, by analogy a geometry of type III (Scheme 1) for the formamido derivatives 3 can be reasonably proposed.

The formation of only one isomer in this case is somewhat surprising as compared to the related thioformamido derivative 2 and may be explained on the basis of a greater stability of one isomer with respect to the other.

The proton spectra of the formamidinato complex **4** show a multiplet at 7.70 ppm due to the CH proton and two singlets at 2.25 and 2.23 ppm of the *p*-tolyl group of the *p*-tolyl-N $\dots$ C(H) $\dots$ N-*p*-tolyl ligand. The magnetic inequivalence of the *p*-tolyl-substituent is confirmed by the <sup>13</sup>C spectra, which show two singlets at 20.8 and 20.4 ppm of the CH<sub>3</sub> groups. In the spectra, a multiplet at 156.8 ppm, which correlates with the proton multiplet at 7.70 ppm in the HMQC experiment, is present and was attributed to the CH carbon resonance of the *p*-tolyl-N $\dots$ C(H) $\dots$ N-*p*-tolyl ligand. Taking into account that in the temperature range between +20 and -80 °C the <sup>31</sup>P spectra appear as a AB<sub>2</sub> multiplet, a type-IV geometry (Scheme 1) for the formamidinato complex **4** can reasonably be proposed.

Mixed-ligand hydrides with PPh<sub>3</sub> and phosphites of the ReH<sub>2</sub>(NO)L(PPh<sub>3</sub>)<sub>2</sub> [10] and ReH<sub>2</sub>(NO)(PPh<sub>3</sub>)<sub>3</sub> [11] type also allowed the synthesis of dithioformato, thioformamido and formamido derivatives after treatment with CF<sub>3</sub>SO<sub>3</sub>H, but, in this case, the stoichiometry of the complexes depends on the nature of the phosphine and of the heteroallene, as shown in Scheme 2.

All the hydrides ReH<sub>2</sub>(NO)L(PPh<sub>3</sub>)<sub>2</sub> and ReH<sub>2</sub>(NO) (PPh<sub>3</sub>)<sub>3</sub> react first with equimolecular amounts of CF<sub>3</sub>SO<sub>3</sub>H to give the ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)L(PPh<sub>3</sub>)<sub>2</sub> and ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)(PPh<sub>3</sub>)<sub>3</sub> intermediates [10], which further react with RNCS (R = Et, *p*-tolyl) to yield the final thioformamido [Re{ $\eta^2$ -RN...-C(H)...S} (NO)L(PPh<sub>3</sub>)<sub>2</sub>]BPh<sub>4</sub> (5, 6) and [Re{ $\eta^2$ -RN...-C(H)...S} (NO)(PPh<sub>3</sub>)<sub>3</sub>]BPh<sub>4</sub> (7) complexes. Surprisingly, the reaction of isocyanate R1NCO (R1 = Ph, *p*-tolyl) with the



 $\kappa^{1}\text{-triflate}$  gives the  $\eta^{2}\text{-formamido}$  derivatives  $\boldsymbol{8}$  and  $\boldsymbol{10}$ only with the ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO){P(OEt)<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub> and  $\text{ReH}(\kappa^1\text{-OSO}_2\text{CF}_3)(\text{NO})(\text{PPh}_3)_3$  precursors. However, with the ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO){PPh(OEt)<sub>2</sub>} (PPh<sub>3</sub>)<sub>2</sub> hydride, containing the PPh(OEt)<sub>2</sub> phosphite ligand, the reaction with isocyanate gives a new complex of the  $[Re{\eta^1-RNC(H)=O}(NO){PPh(OEt)_2}_2(PPh_3)_2]$  $BPh_4$  (9) type whose characterization data suggest the presence of a  $\eta^1$ -coordinate formamido ligand. In this case, the insertion of RNCO is followed by a phosphine exchange between the species, yielding the final complex 9 containing two  $PPh(OEt)_2$  and two  $PPh_3$  ligands. The coordination of the fourth phosphine also suggests that in these complexes the  $\eta^2$ -coordination of the formamido R1NC(H)O is not favored and makes the related complexes unstable, which probably promotes the phosphite exchange giving the more stable  $\eta^1$ -derivative 9.

Carbon disulfide also reacts with the hydride-triflate ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)L(PPh<sub>3</sub>)<sub>2</sub> and ReH( $\kappa^1$ -OSO<sub>2</sub>-CF<sub>3</sub>)(NO)(PPh<sub>3</sub>)<sub>3</sub> intermediates, but in only one case the insertion product [Re{ $\eta^1$ -SC(H)=S}(NO){PPh (OEt)<sub>2</sub>}<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]BPh<sub>4</sub> (11) can be isolated in pure form and characterized (Scheme 3). In the other cases, intractable mixtures of products were always obtained.

Furthermore, we extensively studied the reaction of  $CO_2$  with all the triflate  $ReH(\kappa^1-OSO_2CF_3)(NO)L_3$  complexes (L = phosphites or PPh<sub>3</sub>), and observed that the reaction does proceed, but is slow and often gives unstable complexes. In only one case, a solid sample of the compound was isolated in pure form and characterized as containing the  $\eta^1$ -formate [Re{ $\eta^1$ -OC(H)=O)(NO) {P(OEt)\_3}\_2(PPh\_3)\_2]BPh\_4 (12) derivative (Scheme 3). A phosphite exchange takes place also in these reactions of both  $CO_2$  and  $CS_2$  molecules, giving the



tetrakis(phosphite) derivatives containing the insertion products  $\eta^1$ -coordinated to the metal center.

Finally, 1,3-di-*p*-tolylcarbodiimide reacts with ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)L(PPh<sub>3</sub>)<sub>2</sub> to give the *p*-tolyl-formamidinato complex **13** which, in the case of P(OEt)<sub>3</sub>, was isolated as an orange solid and characterized.

All the complexes **5–13** are stable as solids and in a solution of polar organic solvents, where they behave as 1:1 electrolytes [12]. Their formulation is confirmed by the analytical and spectroscopic data reported in Table 1.

Like the PPh<sub>2</sub>OEt derivatives **2**, the thioformamido  $[\text{Re}\{\eta^2-\text{RN}\cdots\text{C}(H)\cdots\text{S}\}(\text{NO})\text{L}(\text{PPh}_3)_2]\text{BPh}_4$  (**5**, **6**) and  $[\text{Re}\{\eta^2-\text{RN}\cdots\text{C}(H)\cdots\text{S}\}(\text{NO})(\text{PPh}_3)_3]\text{BPh}_4$  (**7**) complexes, containing the PPh<sub>3</sub> ligand, showed the presence of two isomers of the type shown in Scheme 2.

Two multiplets for the CH carbon resonances of RNC(H)S ligand were observed in the <sup>13</sup>C spectra at 187–183 ppm (Table 1), which correlate, in the HMQC experiments, with the two multiplets at 6.90–6.68 ppm due to CH proton resonances observed in the <sup>1</sup>H NMR spectra. In the temperature range between +20 and -80 °C, the <sup>31</sup>P NMR spectra appear as two AB<sub>2</sub> or A<sub>2</sub>B multiplets indicating that in both isomers two phosphines are magnetically equivalent and different from the third. On the basis of these data, the geometry of type V for **5**, **6** and of type VII for **7** may reasonably be proposed.

Depending on the nature of the phosphite ligands, the reaction of isocyanate R1NCO with the mixed-ligand ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub> hydride gives either  $\eta^2$ -RNC(H)O (8, 10) or  $\eta^1$ -RNC(H)O (9) formamido derivatives (Scheme 2). Furthermore, the chelate [Re{ $\eta^2$ -RN...-C(H)...-O}(NO){P(OEt)<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub>]BPh<sub>4</sub> (8) and [Re{ $\eta^2$ -RN...-C(H)...-O}(NO)(PPh<sub>3</sub>)<sub>3</sub>]BPh<sub>4</sub> (10) complexes were obtained as a mixture of two isomers of the type shown in Scheme 2. This hypothesis is sup-

ported by the presence of two CH resonances at 163.3 and 161.9 ppm in the <sup>13</sup>C spectra of **8b** which, in a HMQC experiment, correlate with the two <sup>1</sup>H multiplets near 6.8 ppm due to the CH proton of the RNC(H)O ligand. Furthermore, two AB<sub>2</sub> multiplets were observed in the <sup>31</sup>P spectra, in agreement with the geometries **VIIIA**, **VIIIB** and **XA**, **XB** for the complexes.

The IR spectra of complexes 9 show a medium-intensity band at 1664 (9b) and at 1660  $\text{cm}^{-1}$  (9c) attributable to v(CO) of the  $\eta^1$ -RNC(H)=O ligand. The strong v(NO) band at 1702–1701 cm<sup>-1</sup> is also observed. The <sup>1</sup>H NMR spectra show a multiplet at 6.69 (9b) and at 6.67 (9c) ppm due to the CH signal of the RNC(H)O ligand. The <sup>13</sup>C NMR spectra support the presence of the formamido showing a multiplet at 161.2 ppm (9c) which correlates, in the HMQC experiment, with the proton multiplets at 6.67 ppm. In the temperature range between +20 and  $-80 \,^{\circ}$ C, the  ${}^{31}$ P{ $^{1}$ H} NMR spectra appear as a  $A_2B_2$  multiplet for both the complexes 9band 9c, suggesting the presence of four phosphine ligands two by two magnetically equivalent. The values of the chemical shifts (Table 1) also indicate the presence of both the PPh<sub>3</sub> and PPh(OEt)<sub>2</sub> phosphine ligands, while the value of 22 Hz for  $J_{PP}(J_{AB})$  seems to suggest, by a comparison with the values of related complexes 1-8, that the different phosphines PPh(OEt)<sub>2</sub> and PPh<sub>3</sub> are in a mutually cis position. On the basis of these data, a geometry of the type IX can be tentatively proposed for complexes 9 (Chart 1).

The formation of the tetrakis(phosphine) complexes **9** containing the monodentate formamido ligand may be



Chart 1.  $P = PPh_3$ ,  $L = PPh(OEt)_2$ .

due to the instability of the initial  $[Re{\eta^2-RNC(H)=O}(NO){PPh(OEt)_2}(PPh_3)_2]^+$  complex formed [A], which can give an unstable pentacoordinate intermediate [B] (Scheme 4).

A phosphite exchange between two molecules of this intermediate **[B]** can take place, giving the stable octahedral final complex **9**. Studies on the reaction course show that the product isolated in the initial stage of the reaction (after about 30 min) contains, beside the starting ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)L(PPh<sub>3</sub>)<sub>2</sub> and the final complex **9**, a species supposed to be (by NMR) the chelate [Re{ $\eta^2$ -RNC(H)=O}(NO)L(PPh<sub>3</sub>)<sub>2</sub>]BPh<sub>4</sub> complex **[A]**. The formation of this species and the presence of free phosphite in the reaction mixture support the path proposed in Scheme 4 for the reaction.

The  $\eta^1$ -coordination of the ligand is also observed in both the thioformato [Re{ $\eta^1$ -SC(H)=S}(NO)-{PPh(OEt)\_2}\_2 (PPh\_3)\_2]BPh\_4 (11) and formato [Re-{ $\eta^1$ -OC(H)=O}(NO){PPh(OEt)\_2}\_2(PPh\_3)\_2]BPh\_4 (12) complexes obtained in the reaction of Re( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>) (NO)L(PPh\_3)\_2 with CS<sub>2</sub> and CO<sub>2</sub>, respectively. A reaction path of the type of Scheme 4 may also be invoked in these cases, which lead to the separation of stable complexes of the types of 11 and 12.



 $P = PPh_3, L = PPh(OEt)_2$ 



The presence of the thioformato ligand in **11** is confirmed by the characteristic multiplet of the CH proton of the SC(H)S ligand observed at 6.72 ppm in the proton NMR spectra. The <sup>31</sup>P spectra appear as a  $A_2B_2$  multiplet with  $J_{PP}$  of 22 Hz. On the basis of these data, a geometry of type **XI** like that of the formamido derivatives **9** can reasonably be proposed (Chart 2).

The IR spectrum of the formato [Re{ $\eta^1$ -OC(H)=O} (NO){PPh(OEt)\_2}\_2(PPh\_3)\_2]BPh\_4 (12) complex shows a medium absorption at 1662 cm<sup>-1</sup> attributed to  $v_{as}(CO_2)$ of the  $\eta^1$ -formato ligand. Other  $\eta^1$ -formato complexes show  $v_{as}(CO_2)$  bands in the 1667–1603 cm<sup>-1</sup> range [14], whereas  $\eta^2$ -formato generally show  $v_{as}(CO_2)$  bands [15] between 1585 and 1554 cm<sup>-1</sup>. In the spectra, a strong absorption at 1706 cm<sup>-1</sup> is also observed, due to the v(NO) of the nitrosyl ligand.

The <sup>13</sup>C NMR spectra confirm the presence of the formato ligand showing a broad singlet at 176.8 ppm due to the formato carbon atom. The <sup>1</sup>H spectra do not allow us to clearly assign the formyl CH resonance, due to the overlapping with the phenyl proton signals. However, a HMQC experiment clearly shows the correlation between a signal at 6.73 ppm in the proton NMR spectra and the singlet due to the <sup>13</sup>C formyl carbon resonance at 176.8 ppm, in agreement with the presence of the formato ligand. In the temperature range between +20 and -80 °C, the <sup>31</sup>P spectra appear as a A<sub>2</sub>B<sub>2</sub> multiplet with  $J_{PP}(J_{AB})$  of 22 Hz. On the basis of these data, a geometry of type **XII** (Chart 2) can reasonably be proposed for the formato complex **12**.

Formato complexes obtained by insertion of  $CO_2$ into the metal-hydride bond are of interest as an important chemical step in functionalizing this molecule [1–3]. The preparation of  $[Re(\eta^1-OC(H)=O)(NO)\{PPh-(OEt)_2\}_2(PPh_3)_2]BPh_4$  is a new example involving, for the first time, rhenium as the central metal.

The formamidinato [Re{ $\eta^2$ -*p*-tolylNC(H)N*p*-tolyl} (NO){P(OEt)<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub>]BPh<sub>4</sub> (13) complex was separated as an orange solid containing two isomers. The <sup>1</sup>H NMR spectrum shows, in fact, two CH multiplets at 6.59 and 5.96 ppm, while two AB<sub>2</sub> patterns are present in the  ${}^{31}$ P spectrum. In the proton spectra, two signals at 2.33 and 2.22 ppm for the methyl groups of the *p*-tolyl substituents are also present. On the basis of these data, geometries of types **XIIIA** and **XIIIB** can be proposed for the two isomers of the formamidinato complex **13**.

### 4. Conclusions

In this report, we have highlighted that the use of the hydride-triflate complexes of the ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>) (NO)(PPh<sub>2</sub>OEt)<sub>3</sub> and ReH( $\kappa^1$ -OSO<sub>2</sub>CF<sub>3</sub>)(NO)LP<sub>2</sub> type as precursors allows the facile insertion of heteroallene CS<sub>2</sub>, RNCS, RNCO, and R1NCNR2 into the Re–H bond giving a series of dithioformato, thioformamido, formamido and formamidinato derivatives. The influence of the phosphite ligand on the reactions, yielding either  $\eta^2$ - or  $\eta^1$ -complexes, was also established.

Finally, carbon dioxide inserts into the Re–H bond yielding the stable formato  $[Re{\eta^1-OC(H)=O}(NO)$ {PPh(OEt)<sub>2</sub>}<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]BPh<sub>4</sub> derivative.

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