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Preparation of trihydridostannyl complexes of rhenium stabilised by isocyanide ligands

Gabriele Albertin^{a,*}, Stefano Antoniutti^a, Jesús Castro^b, Gianluigi Zanardo^a

^a Dipartimento di Chimica, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy ^b Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain

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ABSTRACT

Mixed-ligand complexes [ReBr(CO)₂(CNR)_nL_{3-n}] (**1-4**) [R = 4-CH₃OC₆H₄, 4-CH₃C₆H₄, C(CH₃)₃; L = P(OEt)₃, PPh(OEt)₂; *n* = 1, 2] were prepared by allowing carbonyl compounds [ReBr(CO)₄L] and [ReBr(CO)₃L₂] to react with an excess of isocyanide. Treatment of these bromocomplexes [ReBr(CO)₂(CNR)_nL_{3-n}] with SnCl₂ · 2H₂O yielded the trichlorostannyl derivatives [Re(SnCl₃)(CO)₂(CNR)_nL_{3-n}] (**5-8**). Trihydridestannyl complexes [Re(SnH₃)(CO)₂(CNR)_nL_{3-n}] (**9-12**) were prepared by allowing trichlorostannyl compounds **5**-**8** to react with NaBH₄ in ethanol. The trimethylstannyl derivative [Re(SnG₃)(CO)₂(CNC₆H₄-4-CH₃){PPh(OEt)₂}] (**13b**) was also prepared by treating [Re(SnCl₃)(CO)₂(CNC₆H₄-4-CH₃){PPh(OEt)₂}] with an excess of MgBrMe in diethylether. Reaction of the tin trihydride complexes [Re(SnH₃)(CO)₂(CNR)_nL_{3-n}] (**9-12**) with CO₂ (1 atm) led to dinuclear OH-bridging bis(formate) derivatives [Re{Sn(OC(H)=O)₂(µ-OH)}(CO)₂(CNR)_nL_{3-n}]₂ (**14**, **15**). The complexes were characterised spectroscopically (IR, ¹H, ³¹P, ¹³C, ¹¹⁹Sn NMR) and by X-ray crystal structure determination of [Re(SnH₃)(CO)₂{CNC(H₃)₃}PPh(OEt)₂] (**10b**).

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1. Introduction

Transition metal complexes containing stannyl groups SnX_3 and SnR_3 as ligands have been extensively studied in recent years [1–3], not only for the variety of reactions shown both at the metal and at the tin centre, but also because the introduction of a tin ligand into the metal fragment may modify the chemical properties of the complexes and often improve their catalytic activity [1,4].

A large number of mono- and polynuclear stannyl complexes containing halogenostannyl (SnX₃) and organostannyl (SnR₃) ligands have been synthesised [1–3]. However, despite the numerous studies, only recently stable complexes containing the simplest of the tin ligand, the trihydride SnH₃, have been prepared [5] using an osmium(II) fragment of the type [Os(Tp)L(PPh₃)] [Tp = tris(pyrazolyl)borate; L = phosphite] to stabilise the SnH₃ ligand. Further studies from our and other laboratories have pointed out that other d^6 metal fragments, of the type [M(Cp)L(PPh₃)] (M = Ru, Os; L = phosphite), [M(CO)_nL_{5-n}] (M = Mn, Re; n = 2, 3) [5,6] and [Os(κ^2 -S₂CNMe₂)(CO)(PPh₃)₂] [7], are able to stabilise the tin trihydride ligand, and that the reactivity of the SnH₃ group strongly depends on the nature of the ancillary ligands. For example, hydridebis(formate)stannyl complexes [M[SnH{OC(H)=O}₂]-(Cp)L(PPh₃)] are stable and isolable only with the Cp ligand [6c], but with $[M(Tp)L(PPh_3)]$ or with the $[M(CO)_nL_{5-n}]$ fragments the dinuclear OH-bridging bis(formate) derivatives $[[M]-Sn{OC(H)=O}_2(\mu-OH)]_2$ are always obtained [6a,6c].

These results prompted us to extend our study to include isocyanides (CNR) as supporting ligands in the chemistry of tin hydride complexes, to test whether SnH₃ complexes can be prepared with such ligands, and how isocyanide may change the properties of the tin hydride group.

The results of these studies, which include preparation and some reactivity of unprecedented stannyl complexes of rhenium [8] stabilised by isocyanide ligands, are reported here.

2. Experimental

2.1. General considerations

All synthetic work was carried out in an appropriate atmosphere (Ar) using standard Schlenk techniques or an inert atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under nitrogen at -25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Re₂(CO)₁₀ was a Pressure Chemical Co. (USA) product and was used as received. Phosphite PPh(OEt)₂ was prepared by the method of Rabinowitz and Pellon [9], while P(OEt)₃ was an Aldrich product, purified by distillation under nitrogen. Isocyanides CNC₆H₄-4-CH₃ and CNC₆H₄-4-CH₃O were prepared by the



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method of Ziehn and co-workers [10], while CNC(CH₃)₃ was an Aldrich product used as received. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (¹H, ³¹P, ¹³C, ¹¹⁹Sn) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between +20 and -90 °C, unless otherwise noted. ¹H and ¹³C spectra are referred to internal tetramethylsilane; ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄, and ¹¹⁹Sn with respect to Sn(CH₃)₄, and in both cases downfield shifts are considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The swan-mr and INMR software packages [11] were used to treat NMR data. The conductivities of 10^{-3} M solutions of the complexes in CH₃NO₂ 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 complexes $[ReBr(CO)_5]$ and $[ReBr(CO)_3L_2]$ $[L = P(OEt)_3$ and $PPh(OEt)_2]$ were prepared following the methods previously reported [6a,12].

2.2.1. $[ReBr(CO)_4L] [L = P(OEt)_3 (a) and PPh(OEt)_2 (b)]$

A slight excess of the appropriate phosphite (5.2 mmol) was added to a solution of $[ReBr(CO)_5]$ (2 g, 5.0 mmol) in 30 mL of toluene and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (5 mL). A white solid separated out, which was filtered and dried under vacuum [for $[ReBr(CO)_4[P(OEt)_3]]$ (a) 2.42 g, 89%; for $[ReBr(CO)_4[PPh(OEt)_2]]$ (b) 2.62 g, 91%]. *Anal.* Calc. for C₁₀H₁₅BrO₇PRe $[ReBr(CO)_4[P(OEt)_3]]$ (a) (544.31): C, 22.07; H, 2.78. Found: C, 22.19; H, 2.90%. *Anal.* Calc. for C₁₄H₁₅BrO₆PRe $[ReBr(CO)_4[PPh(OEt)_2]]$ (b) (576.35): C, 29.17; H, 2.62. Found: C, 28.98; H, 2.51%.

2.2.2. $[ReBr(CO)_2(CNR)L_2]$ (**1**, **2**) $[R = 4-CH_3OC_6H_4$ (**1**), $C(CH_3)_3$ (**2**); $L = P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

An excess of the appropriate isocyanide (4 mmol) was added to a solution of [ReBr(CO)₃L₂] (2 mmol) in 20 mL of toluene and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (5 mL). The resulting solution was vigorously stirred at 0 °C until a pale yellow solid separated out, which was filtered and dried under vacuum [1.23 g, 78% (**1a**), 1.38 g, 81% (**1b**), 1.33 g, 83% (**2b**)]. *Anal.* Calc. for C₂₂H₃₇BrNO₉P₂Re (**1a**) (787.59): C, 33.55; H, 4.74; Br, 10.15; N, 1.78. Found: C, 33.78; H, 4.83; Br, 10.32; N, 1.64%. *Anal.* Calc. for C₃₀H₃₇BrNO₇P₂Re (**1b**) (851.68): C, 42.31; H, 4.38; N, 1.64. Found: C, 42.48; H, 4.49; N, 1.57%. *Anal.* Calc. for C₂₇H₃₉BrNO₆P₂Re (**2b**) (801.66): C, 40.45; H, 4.90; N, 1.75. Found: C, 40.24; H, 4.95; N, 1.68%.

2.2.3. [$ReBr(CO)_2(CNR)_2L$] (**3**, **4**) [$R = 4-CH_3OC_6H_4$ (**3**), $4-CH_3C_6H_4$ (**4**); $L = P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

An excess of the appropriate isocyanide (8 mmol) was added to a solution of [ReBr(CO)₄L] (2 mmol) in 20 mL of toluene and the reaction mixture refluxed for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (5 mL). A pale yellow solid separated out, which was filtered and dried under vacuum [1.36 g, 90% (**3a**), 1.39 g, 92% (**4b**)]. *Anal.* Calc. for C₂₄H₂₉BrN₂O₇PRe (**3a**) (754.58): C, 38.20; H, 3.87; Br, 10.59; N, 3.71. Found: C, 38.02; H, 3.76; Br, 10.75; N, 3.84%. *Anal.* Calc. for C₂₈H₂₉BrN₂O₄PRe (**4b**) (754.63): C, 44.57; H, 3.87; N, 3.71. Found: C, 44.74; H, 3.75; N, 3.63%. 2.2.4. $[Re(SnCl_3)(CO)_2(CNR)L_2]$ (**5**, **6**) $[R = 4-CH_3OC_6H_4$ (**5**), $C(CH_3)_3$ (**6**); $L = P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

In a 100-mL three-necked round-bottomed flask were placed solid samples of $[ReBr(CO)_2(CNR)L_2]$ (**1**, **2**) (1.5 mmol), an excess of $SnCl_2 \cdot 2H_2O$ (6 mmol, 1.35 g) and 30 mL of ethanol. The reaction mixture was refluxed for 2 h and then the solution was concentrated by evaporation under reduced pressure to about 5 mL. The yellow solid that separated out was isolated by filtration and crystallised from CH_2Cl_2 and ethanol [1.08 g, 77% (**5a**), 1.18 g, 79% (**5b**), 1.19 g, 84% (**6b**)]. *Anal.* Calc. for $C_{22}H_{37}Cl_3NO_9P_2ReSn$ (**5a**) (932.75): C, 28.33; H, 4.00; Cl, 11.40; N, 1.50. Found: C, 28.16; H, 4.11; Cl, 11.24; N, 1.62%. *Anal.* Calc. for $C_{20}H_{37}Cl_3NO_7P_2ReSn$ (**5b**) (996.84): C, 36.15; H, 3.74; Cl, 10.67; N, 1.41. Found: C, 36.21; H, 3.85; Cl, 10.39; N, 1.27%. *Anal.* Calc. for $C_{27}H_{39}Cl_3NO_6P_2ReSn$ (**6b**) (946.83): C, 34.25; H, 4.15; Cl, 11.23; N, 1.48. Found: C, 34.36; H, 4.02; Cl, 11.40; N, 1.32%.

2.2.5. $[Re(SnCl_3)(CO)_2(CNR)_2L]$ (**7**, **8**) $[R = 4-CH_3OC_6H_4$ (**7**), $4-CH_3C_6H_4$ (**8**); $L = P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

These complexes were prepared following the method used for **5**, **6**, starting from [ReBr(CO)₂(CNR)₂L] (**3**, **4**) (1.5 mmol) [1.00 g, 74% (**7a**), 1.02 g, 78% (**8a**), 1.07 g, 79% (**8b**)]. *Anal.* Calc. for $C_{24}H_{29}Cl_3N_2O_7PReSn$ (**7a**) (899.75): C, 32.04; H, 3.25; Cl, 11.82; N, 3.11. Found: C, 32.28; H, 3.41; Cl, 11.77; N, 3.28%. *Anal.* Calc. for $C_{24}H_{29}Cl_3N_2O_5PReSn$ (**8a**) (867.75): C, 33.22; H, 3.37; Cl, 12.26; N, 3.23. Found: C, 33.05; H, 3.52; Cl, 12.03; N, 3.39%. *Anal.* Calc. for $C_{28}H_{29}Cl_3N_2O_4PReSn$ (**8b**) (899.79): C, 37.38; H, 3.25; Cl, 11.82; N, 3.11. Found: C, 37.16; H, 3.12; Cl, 11.97; N, 3.02%.

2.2.6. $[Re(SnH_3)(CO)_2(CNR)L_2]$ (9, 10) $[R = 4-CH_3OC_6H_4$ (9), $C(CH_3)_3$ (10); $L = P(OEt)_3$ (a), $PPh(OEt)_2$ (b)]

An excess of NaBH₄ (20 mmol, 0.76 g) in ethanol (20 mL) was added to a suspension of the appropriate trichlorostannyl complex $[Re(SnCl_3)(CO)_2(CNR)L_2]$ (5, 6) (1 mmol) in ethanol (20 mL) and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure to give a solid, from which the [M]-SnH₃ complex was extracted with three 30-mL portions of toluene. The extracts were evaporated to drvness, leaving an oil which was triturated with ethanol (3 mL). A white solid separated out from the resulting solution cooled to -20 °C, which was isolated by filtration and crystallised from toluene and hexane [0.54 g, 65% (9a), 0.63 g, 71% (9b), 0.57 g, 68% (10b)]. Anal. Calc. for C₂₂H₄₀NO₉P₂ReSn (**9a**) (829.42): C, 31.86; H, 4.86; N, 1.69. Found: C, 31.71; H, 4.98; N, 1.57%. Anal. Calc. for C₃₀H₄₀NO₇P₂ReSn (9b) (893.51): C, 40.33; H, 4.51; N, 1.57. Found: C, 40.51; H, 4.66; N, 1.51%. Anal. Calc. for C₂₇H₄₂NO₆P₂ReSn (**10b**) (843.49): C, 38.45; H, 5.02; N, 1.66. Found: C, 38.68; H, 4.95; N, 1.52%.

2.2.7. $[Re(SnH_3)(CO)_2(CNR)_2L]$ (11, 12) $[R = 4-CH_3OC_6H_4$ (11), 4-CH₃C₆H₄ (12); $L = P(OEt)_3$ (**a**), PPh(OEt)₂ (**b**)]

These complexes were prepared exactly like the monoisocyanide derivatives **9**, **10**, starting from $[\text{Re}(\text{SnCl}_3)(\text{CO})_2(\text{CNR})_2\text{L}]$ (**7**, **8**) (1 mmol) [0.61 g, 77% (**11a**), 0.55 g, 72% (**12a**), 0.62 g, 78% (**12b**)]. *Anal.* Calc. for C₂₂H₄₀NO₉P₂ReSn (**11a**) (796.41): C, 36.19; H, 4.05; N, 3.52. Found: C, 36.34; H, 3.97; N, 3.70%. *Anal.* Calc. for C₂₄H₃₂N₂O₅PReSn (**12a**) (764.41): C, 37.71; H, 4.22; N, 3.66. Found: C, 37.52; H, 4.36; N, 3.49%. *Anal.* Calc. for C₂₈H₃₂N₂O₄PReSn (**12b**) (796.46): C, 42.22; H, 4.05; N, 3.52. Found: C, 42.02; H, 4.18; N, 3.37%.

2.2.8. $[Re(SnMe_3)(CO)_2(CNC_6H_4-4-CH_3O)\{PPh(OEt)_2\}_2]$ (13b)

An excess of MgBrMe (1.5 mmol, 0.5 mL of a 3 M solution in diethyl ether) was added to a suspension of the trichlorostannyl complex [Re(SnCl₃)(CO)₂(CNC₆H₄-4-CH₃O){PPh(OEt)₂}₂] (**5b**) (0.25 mmol, 0.25 g) in 25 mL of diethyl ether cooled to $-196 \,^{\circ}$ C. The reaction mixture was brought to room temperature and stirred

for 2 h and then the solvent was removed under reduced pressure. Ethanol (10 mL) was added to the obtained solid and the resulting suspension was stirred for 1 h. The solvent was evaporated to give a solid, from which the trimethylstannyl complex was extracted with three 10-mL portions of toluene. The extracts were evaporated to dryness leaving an oil, which was triturated with ethanol (3 mL). A pale yellow solid slowly separated out from the resulting solution, which was isolated by filtration and crystallised from ethanol [0.12 g, 50%]. *Anal.* Calc. for $C_{33}H_{46}NO_7P_2ReSn$ (935.59): C, 42.36; H, 4.96; N, 1.50. Found: C, 42.56; H, 5.13; N, 1.39%.

2.2.9. $[Re{Sn(OC(H)=O)_2(\mu-OH)}(CO)_2(CNC_6H_4-4-CH_3O){P(OEt)_3}_2]_2$ (14a) and $[Re{Sn(OC(H)=O)_2(\mu-OH)}(CO)_2(CNC_6H_4-4-CH_3)_2{P(OEt)_3}]_2$ (15a)

A solution of the appropriate trihydridostannyl complex [Re $(SnH_3)(CO)_2(CNR)_{3-n}{P(OEt)_3}_n$] (n = 1, 2) (**9a**, **12a**) (0.1 mmol) in toluene (5 mL) was stirred under a CO₂ atmosphere (1 atm) at room temperature for 3 h. The solvent was removed under reduced pressure to give an oil, which was triturated with hexane (5 mL) and ethanol (0.5 mL). A white solid slowly separated out, which was isolated by filtration and crystallised from toluene and hexane [0.14 g, 76% (14a), 0.13 g, 73% (15a)]. Anal. Calc. for C₄₈H₈₀N₂O₂₈₋P₄Re₂Sn₂ (**14a**) (1866.87): C, 30.88; H, 4.32; N, 1.50. Found: C, 30.64; H, 4.44; N, 1.63%. Anal. Calc. for C₅₂H₆₄N₄O₂₀P₂Re₂Sn₂ (**15a**) (1736.86): C, 35.96; H, 3.71; N, 3.23. Found: C, 36.18; H, 3.84; N, 3.09%.

2.2.10. X-ray crystal structure determination of [Re(SnH₃)(CO)₂{CNC(CH₃)₃}{PPh(OEt)₂}₂] (**10b**)

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo, Spain) using graphite monochromated Mo K α radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART [13] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [14] for integration of intensity of reflections and scaling, and sadabs [15] for empirical absorption correction. The structure was solved and refined with the oscall program [16] by direct methods and refined by a full-matrix least-squares based on F^2 [17]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters, except those bonded to the tin atom that were found in the density map and refined isotropically, although one restrain was applied to one of them in order to maintain the distance Sn-H within chemically accepted values. Details of crystal data and structural refinement are given in Table 1.

3. Results and discussion

3.1. Preparation of isocyanide complexes

Mixed-ligand isocyanide complexes $[\text{ReBr}(\text{CO})_2(\text{CNR})L_2]$ (1, 2) and $[\text{ReBr}(\text{CO})_2(\text{CNR})_2L]$ (3, 4) were prepared by substituting carbonyl ligands in the $[\text{ReBr}(\text{CO})_nL_{5-n}]$ (n = 3, 4) precursors, as shown in Scheme 1.

Tricarbonyl complexes [ReBr(CO)₃L₂] react with isocyanide CNR in refluxing toluene to give the mixed-ligand monoisocyanide derivatives [ReBr(CO)₂(CNR)L₂] (**1**, **2**) in good yields.

Under the same conditions, tetracarbonyl species $[ReBr(CO)_4L]$ react with isocyanide CNR to give bis(isocyanide) derivatives $[ReBr(CO)_2(CNR)_2L]$ (**3**, **4**), which were isolated and characterised (Scheme 1). The reaction was also carried out with a larger excess of isocyanide and for a longer reaction time, but no further ligand substitution was observed, as the bis(isocyanide) derivatives **3** and **4** were the only formed products.

Table 1

Crystal data and structure refinement for 10b.

Empirical formula	C ₂₇ H ₄₂ NO ₆ P ₂ ReSn
Formula weight	843.45
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	
a (Å)	16.5551(15)
b (Å)	15.4486(14)
<i>c</i> (Å)	26.990(3)
V (Å ³)	6902.8(11)
Ζ	8
D_{calc} (Mg/m ³)	1.623
Absorption coefficient (mm ⁻¹)	4.356
F(000)	3312
Crystal size (mm)	$0.44 \times 0.43 \times 0.10$
Theta range for data collection (°)	1.51-25.03
Index ranges	$-19\leqslant h\leqslant 19;\ -18\leqslant k\leqslant 11;$
	$-31 \leq l \leq 32$
Reflections collected	22 522
Independent reflections [R _{int}]	5511 [0.0854]
Reflections observed (> 2σ)	2846
Data completeness	0.905
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	1.000 and 0.484
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5511/0/361
Goodness-of-fit (GOF) on F ²	0.980
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0647 \ wR_2 = 0.1615$
R indices (all data)	$R_1 = 0.1309 \ wR_2 = 0.1840$
Largest difference in peak and hole	1.601 and -2.168
(e Å ⁻³)	



$$\begin{split} R &= 4\text{-}CH_3OC_6H_4 \ (\textbf{1,3}), \ C(CH_3)_3 \ (\textbf{2}), \ 4\text{-}CH_3C_6H_4 \ (\textbf{4}); \\ L &= P(OEt)_3 \ (\textbf{a}), \ PPh(OEt)_2 \ (\textbf{b}). \end{split}$$

Scheme 1.

Good analytical data were obtained for the isocyanide complexes **1–4**, which were isolated as pale yellow solids stable in air and in solution of common organic solvents, in which they behave as non-electrolytes [18].

Infrared spectra and ¹H, ³¹P and ¹³C NMR data (Tables 2 and 3) support the proposed formulations for the complexes and allow type I and II geometries (Scheme 1) to be established in solution.

The IR spectra of the monoisocyanide derivatives **1** and **2** show only one band at 2134–2177 cm⁻¹ due to v_{CN} of isocyanide and two strong absorptions at 1967–1962 and at 1894–1870 cm⁻¹ attributed to v_{CO} of the two carbonyl ligands in a mutually *cis* position. At temperatures between +20 and -80 °C, the ³¹P{¹H} NMR spectra display only one singlet, matching the magnetic equivalence of the two phosphite ligands. Besides the signals of the substituents of both phosphite and isocyanide ligands, the ¹³C NMR spectra show, two triplets at

Table 2

Selected IR and NMR data for rhenium complexes.

Compound	IR ^a		¹ H NMR ^b			³¹ P{ ¹ H} NMR ^{b,c}
	cm ⁻¹	Assgnt	ppm; J, Hz	Assgnt	Spin syst	ppm; J, Hz
1a [ReBr(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){P(OEt) ₃ } ₂]	2134 s	v _{cn}	7.33–6.86 m	Ph	A ₂	115.5 s
	1967 s	vco	4.14	CH ₂		
	1894 s		3.81 s	CH ₃ isocy		
1b $[P_{PBr}(CO) (CNC H A CH O)(PDb(OEt))]$	2148 c		1.30 t 7.75 m	CH ₃ pnos	Δ	131 Q c
$ID [Red(CO)_2(CNC_6H_4-4-CH_3O)[FFII(OEL)_2]_2]$	2140 S 1962 s	V _{CN}	7.75 m	FII	R2	151.9 5
	1877 s	VLO	6.71 d			
			6.51 d			
			4.31 m	CH ₂		
			4.08 m			
			3.98 m			
			3.85 m	CIL isoar		
			3.77 III 1 35 t	CH ₃ ISOCY		
			1.31 t	cris phos		
2b $[\text{ReBr}(\text{CO})_2(\text{CN}^t\text{Bu})\{\text{PPh}(\text{OEt})_2\}_2]$	2177 s	v _{cn}	7.77-7.35 m	Ph	A ₂	132.0 s
	1962 s	vco	4.25 m	CH ₂		
	1870 s		4.04 m			
			3.92 m			
			3./8 m	CII phos		
			1.55 L 1.79 t	CH ₃ phos		
			1.02 s	CH ₂ isocv		
3a [ReBr(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O) ₂ {P(OEt) ₃ }]	2161 s	VCN	7.40–6.90 m	Ph	А	117.2 s
	2122 s		4.14 m	CH ₂		
	1970 s	v _{co}	3.82 s	CH ₃ isocy		
	1894 s		1.33 t	CH ₃ phos		
4b [ReBr(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {PPh(OEt) ₂ }]	2156 s	V _{CN}	7.80–6.48 m ^u	Ph	A	131.8 s ^u
	2118 S		4.30 m	CH ₂		
	1892 s	VCO	2 38 s m	CH ₂ isocv		
	1002 0		2.37 s	engiboey		
			1.34 t	CH ₃ phos		
			1.32 t			
5a $[Re(SnCl_3)(CO)_2(CNC_6H_4-4-CH_3O){P(OEt)_3}_2]$	2152 s	v _{cn}	7.42–6.93 m ^e	Ph	A ₂	δ _A 117.0 ^e
	1984 s	v _{co}	4.09 m	CH ₂		$\int_{31 \text{ P}^{117} \text{ Sn}} = 286.8$
	1940 s		3.83 S	CH ₃ ISOCY		
5b [Re(SpCl ₂)(CO) ₂ (CNC ₂ H ₄ -4-CH ₂ O){PPb(OFt) ₂ } ₂]	2151 s	VcN	7 75–6 78 m ^d	Ph	Aa	δ. 136 3 ^d
	1988 s	Vco	4.10–3.85 m	CH ₂	••2	$I_{31P117sp} = 248.5$
	1937 s		3.80 s	CH ₃ isocy		9 I 5II
			1.39 t	CH ₃ phos		
			1.37 t			
6b $[\text{Re}(\text{SnCl}_3)(\text{CO})_2(\text{CN}^{1}\text{Bu})\{\text{PPh}(\text{OEt})_2\}_2]$	2149 s	v _{cn}	7.78–7.41 m	Ph	A ₂	δ _A 136.6
	1986 s	vco	4.02 m	CH ₂		$\int_{31} p_{117} Sn = 251.8$
	1941 5		3.97 III 3.90 m			
			1 40 t	CH ₂ phos		
			1.35 t	eng phot		
			1.11 s	CH ₃ isocy		
7a $[Re(SnCl_3)(CO)_2(CNC_6H_4-4-CH_3O)_2{P(OEt)_3}]$	2165 s	v _{CN}	7.46 m	Ph	А	167.5 s
	2135 s		6.93 m			$J_{^{31}P^{117}Sn} = 292.5$
	1989 s	v _{co}	4.08 q	CH ₂		
	1952 \$		3.82 c	CH ₃ ISOCY		
			1 34 t	CH ₂ phos		
8a [Re(SnCl ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {P(OEt) ₃ }]	2172 s	VCN	7.40-7.21	Ph	А	117.0
	2142 s		4.08 qnt	CH ₂		$J_{31P^{117}Sn} = 295.5$
	1986 s	v _{co}	2.38 s	CH ₃ isocy		
	1941 s		2.37 s			
9b $[P_0(S_DC])(CO)$ (CNC H 4 CU) (DDb((DEt)))	2166 -		1.34 t	CH ₃ phos	٥	126.2
ou $[\text{Re}(3)(\text{U})_2(\text{U})_6\pi_4-4-\text{U}H_3)_2\{\text{PPn}(\text{U}\text{E}t)_2\}]$	2100 S	VCN	4.04 m	CH	Λ	130.2 S
	1987 s	Vco	2.40 s	CH ₂ isocv		J31p11/Sn - 240.0
	1950 s		1.23 t	CH ₃ phos		
9a [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){P(OEt) ₃ } ₂]	2118 s	v _{cn}	7.36-7.01 m ^e	Ph	A ₂	123.1 s ^e
	1956 s	v _{co}	4.01 m	CH ₂		$J_{^{31}P^{117}Sn} = 199.5$
	1902 s		3.84 s	CH ₃ isocy		
	1757 br	v _{SnH}	A ₂ MX ₃	SnH ₃		
			∂ _X 2.85			
			$J_{AX} = 5.0$ $J_{10117c_1} = 1157$			
			1.27 t	CH ₃ phos		
				- 1		

Table 2 (continued)

Compound	IR ^a		¹ H NMR ^b			³¹ P{ ¹ H} NMR ^{b,c}
	cm ⁻¹	Assgnt	ppm; J, Hz	Assgnt	Spin syst	ppm; J, Hz
9b [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){PPh(OEt) ₂ } ₂]	2127 s 1948 s 1188 s	v _{cn} v _{co}	7.84–6.31 m ^d 3.99 m 3.75 s	Ph CH ₂ CH ₂ isocy	A ₂	139.8 s ^d $J_{31p117} = 168.5$
	1775 s 1744 s	v _{SnH}	A_2MX_3 $\delta_X 3.5$ $J_{AX} = 3.1$ 1175	SnH ₃		
			$J_{1H^{117}Sn} = 1175$ 1.17 t	CH ₃ phos		
10b $[Re(SnH_3)(CO)_2(CN^tBu){PPh(OEt)_2}_2]$	2141 s	v _{cn}	7.83–7.02 m ^d	Ph	A ₂	140.0 s ^d
	1902 s	VCO	3.87 m	CH ₂		$J_{31}p_{117}Sn = 175.9$
	1741 br	v _{SnH}	3.66 m A_2MX_3 δ_X 3.33	SnH ₃		
			J_{MX} = 3.4 $J_{^{1}H^{117}Sn}$ = 1147.5 1.19 t	CH ₃ phos		
			1.12 t	CIL isoau		
11a [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O) ₂ {P(OEt) ₃ }]	2143 s	VCN	0.74 s 7.43–7.00 m ^e	Ph	А	124.4 s ^e
	2105 s		4.03 qnt	CH ₂		$J_{^{31}P^{117}Sn} = 194.0$
	1971 s 1915 s	v _{co}	3.85 S AMX ₃	CH_3 isocy SnH ₃		
	1760 m	v _{SnH}	δ _X 2.89			
	1736 m		$J_{AX} = 3.5$ $J_{14117s_{P}} = 1143.2$			
			1.29 t	CH ₃ phos		
12a $[\text{Re}(\text{SnH}_3)(\text{CO})_2(\text{CNC}_6\text{H}_4\text{-}4\text{-}\text{CH}_3)_2(\text{P}(\text{OEt})_3)]$	2139 s	v _{CN}	7.32 m ^e	Ph CH-	A	124.2 s ^{e,r}
	1966 s	vco	2.37 s	CH ₂ CH ₃ isocy		$J_{31}p_{11}s_{n} = 154.5$
	1933 s		AMX ₃	SnH ₃		
	1759 DI	VSnH	$J_{AX} = 3.7$			
			$J_{^{1}H^{117}Sn} = 1164.6$	av. 1		
12b $[Re(SnH_3)(CO)_5(CNC_6H_4-4-CH_3)_5(PPh(OEt)_3)]$	2135 s	VCN	1.28 t 7.76–7.01 m ^e	CH_3 pnos Ph	А	138.7 s ^e
5/2(()2)]	2092 s	civ	4.05 m	CH ₂		$J_{^{31}P^{117}Sn} = 171$
	1956 s 1910 s	vco	3.83 m 2.36 s	CH ₂ isocv		
	1756 s, br	v _{SnH}	2.34 s			
			AMX ₃ δ ₂ 2 91	SnH ₃		
			$J_{AX} = 3.3$			
			$J_{^{1}H^{^{117}Sn}} = 1162.0$	CH- phos		
			1.33 t	CH3 phos		
13b [Re(SnMe ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){PPh(OEt) ₂ } ₂]	2135 s	v _{cn}	7.68–6.53 m ^e	Ph	A ₂	141.0 s ^e
	1957 s 1902 s	VCO	3.80 m	CH ₂		$J_{31}p_{117}Sn = 141.5$
			3.70 m	CIL in a		
			3.78 s 1.33 t	CH_3 isocy CH_3 phos		
			1.29 t	6 M		
			0.084 s $I_{1H119Sp} = 35.7$	Snivie ₃		
			$J_{1H^{117}Sn} = 34.1$			
14a $[\text{Re}\{\text{Sn}(OC(H)=0)_2(\mu=0H)\}(CO)_2(CNC_6H_4=4-CH_3O)\{P(OEt)_3\}_2]_2$	2148 s 1981 s	V _{CN}	8.52 s° 7 64 d	HC=O Ph	A ₂	118.7^{e}
	1922 s	.00	7.01 d			J31p11311
	1673 m 1602 m	v _{oco}	4.14 m 3.86 s	CH ₂ CH ₂ isocy		
	1002 111		1.32 t	CH ₃ phos		
			8.63 s ^t 8 31 s ^f	OH HC=0		
15a [Re{Sn(OC(H)=O) ₂ (µ-OH)}(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {P(OEt) ₃ }] ₂	2162 s	VCN	8.49 s	HC=0	А	119.8
	2127 s	v	7.44-7.10 m	Ph		$J_{^{31}P^{117}Sn} = 308.0$
	1938 s	VCO	2.37 s	CH_2 CH_3 isocy		
	1653 m	voco	2.36 s	CII I	А	
	1592 m		1.30 t 8.61 s ^f	CH ₃ phos OH		
			8.26 s ^f	HC=O		

 $\label{eq:constraint} \begin{array}{l} ^{a} \mbox{ In KBr pellets.} \\ ^{b} \mbox{ In CD}_2Cl_2 \mbox{ at 20 °C, unless otherwise noted.} \\ ^{c} \mbox{ Positive shifts downfield from 85\% H}_3PO_4. \\ ^{d} \mbox{ In CD}_3C_6D_5. \\ ^{e} \mbox{ In (CD}_3)_2CO. \\ ^{f} \mbox{ At } -70 \ ^{o}C. \end{array}$

Table 3 $^{13}C\{^{1}H\}$ and ^{119}Sn NMR data for selected rhenium complexes.

Compound ^a	13C{1H} NMR		¹¹⁹ Sn NMR	
	ppm; J, Hz	Assgnt	Spin syst	ppm; J, Hz
1b [ReBr(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){PPh(OEt) ₂ } ₂]	196.1 t	СО		
	$J_{\rm CP} = 11.5$			
	190.2 t			
	$J_{CP} = 9.75$	Pl		
	160-114 m 152.0 t.br	Ph		
	63.0 t	CHa		
	62.6 t	chi		
	55.9 s	CH₃O		
	16.3 t	CH ₃ phos		
2b $[\text{ReBr}(\text{CO})_2(\text{CN}^t\text{Bu})\{\text{PPh}(\text{OEt})_2\}_2]$	195.9 t	CO		
	$J_{\rm CP} = 12.5$			
	190.7 t			
	$J_{CP} = 11.2$ 141.6 br	CN		
	141–128 m	Ph		
	62.8 t	CH ₂		
	62.4 t			
	57.0 s	<i>C</i> (CH ₃)		
	30.0 s	C(CH ₃)		
$2 = \left[\mathbf{D}_{\mathbf{r}} \mathbf{D}_{\mathbf{r}} (\mathbf{C} \mathbf{O}) \left(\mathbf{C} \mathbf{N} \mathbf{C} \mathbf{H} + \mathbf{A} \mathbf{C} \mathbf{H} \mathbf{O} \right) \left(\mathbf{D} (\mathbf{O} \mathbf{C} \mathbf{h}) \right) \right]$	16.3 t	CH_3 phos		
3a [ReBr(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O) ₂ { $P(OET)_3$ }]	192.4 d L = 12.0	CO		
	188 7 d			
	$I_{CP} = 11.3$			
	160–114 m	Ph		
	148.7 d	CN		
	$J_{\rm CP} = 21$			
	147.5 d			
	$J_{CP} = 96$	<u>cu</u>		
	56.0 s			
	55.9 s	chijo		
	16.3 d	CH_3 phos		
4b [ReBr(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {PPh(OEt) ₂ }]	192.9 d ^b	CO		
	J _{CP} = 11.5			
	189.1 d			
	$J_{CP} = 9.5$	CN		
	149.2 DI 140–126 m	Ph		
	63.0 d	CH ₂		
	21.4 s	$CH_3 p$ -tolyl		
	16.4 d	CH ₃ phos		
5a $[\text{Re}(\text{SnCl}_3)(\text{CO})_2(\text{CNC}_6\text{H}_4\text{-}4\text{-}\text{CH}_3\text{O})\{\text{P}(\text{OEt})_3\}_2]$	192.3 t ^c	CO	A ₂ M ^c	δ_{M} –144.7
	$J_{\rm CP} = 11.3$			$J_{\rm AM} = 299.6$
	189.6 t			
	$J_{CP} = 11.7$ 160.6-115.2 m	Dh		
	145.2 t br	CN		
	69.6 t	CH ₂		
	56.1 s	CH ₃ O		
	16.1 t	CH ₃ phos		
5b $[\text{Re}(\text{SnCl}_3)(\text{CO})_2(\text{CNC}_6\text{H}_4\text{-}4\text{-}\text{CH}_3\text{O})\{\text{PPh}(\text{OEt})_2\}_2]$	194.1 t ^b	CO	A ₂ M ^b	δ_{M} –141.6
	$J_{\rm CP} = 10.9$			$J_{AM} = 259.0$
	189.9 t			
	$J_{CP} = 5.7$ 160–128 m	Ph		
	147.2 br	CN		
	64.1 t	CH ₂		
	56.1 s	CH ₃ O		
	16.3 t	CH ₃ phos		
6D [Re(SnCl ₃)(CO) ₂ (CN'Bu){PPh(OEt) ₂ } ₂]	193.4 t	CO	A ₂ M	$\delta_{\rm M} - 143.0$
	$J_{CP} = 10.9$			$J_{AM} = 263.7$
	$I_{cp} = 9.6$			
	140.5–128.6 m	Ph		
	134.9 br	CN		
	63.7 t	CH ₂		
	58.5 s	$C(CH_3)$		
	29.8 s	C(CH ₃)		
	16.1 t	CH_3 phos		

Table 3 (continued)

Compound ^a	¹³ C{ ¹ H} NMR		¹¹⁹ Sn NMR	
	ppm; J, Hz	Assgnt	Spin syst	ppm; J, Hz
7a [Re(SnCl ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O) ₂ {P(OEt) ₃ }]	190.1 d J _{CP} = 11.6 188.4 d	CO	AM	$\delta_{\rm M} - 139.5$ $J_{\rm AM} = 304.5$
	J _{CP} = 10.9 160–115 m 142.6 d J _{CP} = 12 140.6 d	Ph CN		
	$J_{CP} = 72$ 62.8 d 56.1 s 56.0	CH ₂ CH ₃ O		
8a [Re(SnCl ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {P(OEt) ₃ }]	16.2 d	CH ₃ phos	АМ	$\delta_{\rm M} - 138.3$
8b [Re(SnCl ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {PPh(OEt) ₂ }]	190.8 d $J_{CP} = 10.6$ 188.2 d $I_{CP} = 9.2$	СО	АМ	$\delta_{\rm M} = 307.3$ $\delta_{\rm M} = 134.3$ $J_{\rm AM} = 259.0$
	144.3 br 140–126 m 64.1 d 21.5 s	CN Ph CH ₂ CH ₃ p-tolyl CH, phor		
9a [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){P(OEt) ₃ } ₂]	$ 198.7 t^{c} \\ J_{CP} = 12 \\ 193.3 t \\ J_{CP} = 10 $	CO	$A_2MX_3^c$	$\delta_{\rm M} - 493.5$ $J_{\rm AM} = 207.4$ $J_{\rm AX} = 3.6$ $J_{\rm MX} = 1210.8$
	153.8 t, br 160–115 m 61.6 t 56.0 s 16.2 t	CN Ph CH ₂ CH ₃ O CH ₃ D		
9b [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){PPh(OEt) ₂ } ₂]	$J_{CP} = 11.8$ $J_{CP} = 9.3$	CO	A ₂ MX ₃ ^b	$\delta_{M} - 477.0$ $J_{AM} = 175.0$ $J_{AX} = 3.1$ $J_{MX} = 1229.7$
	156.7 t, br 159–114 m 62.3 d 54.9 s	CN Ph CH ₂ CH ₃ O CH, phos		
10b [Re(SnH ₃)(CO) ₂ (CN ^t Bu){PPh(OEt) ₂ } ₂]	$199.4 t^{b}$ $J_{CP} = 11.6$ 193.5 t $J_{CP} = 9.4$	CO	A ₂ MX ₃ ^b	$\delta_{\rm M} = 477.3$ $J_{\rm AM} = 183.1$ $J_{\rm MX} = 1202.9$
	143.8 br 142–124 m 61.9 t 56.2 s 30.1 s	CN Ph CH ₂ C(CH ₃) C(CH ₃)		
11a [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O) ₂ {P(OEt) ₃ }]	15.9 t	CH₃ phos	AMX ₃ ^c	$\delta_{\rm M} - 489.5$ $J_{\rm AM} = 202.0$ $J_{\rm AX} = 3.5$
12a [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {P(OEt) ₃ }]	196.5 d ^{c,d} $J_{CP} = 10.5$ 191.7 d $I_{CP} = 9.8$	со	AMX ₃ ^c	$J_{MX} = 1197.5$ $\delta_M -501.5$ $J_{AM} = 202.5$ $J_{AX} = 3.7$ $L_{XY} = 1218.5$
	151.9 br 149.0 br 140–114 m	CN Ph		JMX 121010
	62.7 d 20.9 s 20.3 s	CH ₂ CH ₃ <i>p</i> -tolyl		
	16.1 d	CH ₃ phos		continued or much a
			((continued on next page)

Table 3 (continued)

Compound ^a	13C{1H} NMR		¹¹⁹ Sn NMR	
	ppm; J, Hz	Assgnt	Spin syst	ppm; J, Hz
12b [Re(SnH ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃) ₂ {PPh(OEt) ₂ }]	197.35 d ^c	CO	AMX ₃ ^c	$\delta_{\rm M}$ –479.4
	$J_{\rm CP} = 11$			$J_{AM} = 178$
	192.4 d			$J_{AX} = 3.3$
	$J_{\rm CP} = 10$			J _{MX} = 1201.5
	152.6 br	CN		
	152.0 d			
	$J_{\rm CP} = 37.7$			
	142–113 m	Ph		
	62.9 d	CH ₂		
	21.2 s	$CH_3 p$ -tolyl		
	16.3 d	CH_3 phos		
13b [Re(SnMe ₃)(CO) ₂ (CNC ₆ H ₄ -4-CH ₃ O){PPh(OEt) ₂ } ₂]	202.8 t ^c	CO	A ₂ MX ₉ ^c	$\delta_{\rm M}$ –98.0
	$J_{\rm CP} = 11.7$			$J_{AM} = 147.5$
	195.0 t			$J_{MX} = 35.7$
	$J_{\rm CP} = 9.8$			5.000
	157.5 t	CN		
	$I_{CP} = 6.0$			
	160–115 m	Ph		
	62.5 t	CH ₂		
	55.9 s	CH ₂ O		
	165 t	CH ₂ phos		
	-4.53 s	CH ₂ Sn		
	$J_{13}c_{19}c_{19} = 156.5$			
	$J_{\rm Herror} = 150.0$			
14a $[\text{Re}\{\text{Sn}(\mu-OH)(OC(H)=O)_{2}\}(CO)_{2}(CNC_{2}H_{4}-4-CH_{2}O)\{P(OEt)_{2}\}_{2}]_{2}$	$193.1 t^{c}$	0	A ₂ M ^c	$\delta_{M} = 496.0$
	$I_{cn} = 11.5$	20		$I_{\rm M} = 328$
	191 0 t			JAM 520
	$I_{cn} = 10.8$			
	166 9 s	C(H)=0		
	160_115 m	Ph		
	155.8 br	CN		
	62.6 t	CH-		
	56.0 c			
	16 4 t	CH, phos		
$15_2 \left[P_0(S_p(\mu, \Theta H)(\Theta C(H) - \Theta)_{-})(C \Theta)_{-}(C N C_{-} H, A_{-} C H_{-})_{-} (P(\Theta E_{+})_{-}) \right]_{-}$	10.4 t		AM	5. 1922
$15a [Re{SII(\mu-OH)(OC(H)-O)_2}(CO)_2(CNC_6H_4-4-CH_3)_2[P(OEI)_3]]_2$	I = 12.0	0	Alvi	$o_{\rm M} = 465.5$
	$J_{CP} = 12.0$			J _{AM} – 519.5
	189.0 0			
	$J_{CP} = 11.5$	C(U)-0		
	107.0 5	C(H)=0		
	144.3 0	CIN		
	$J_{CP} = 15$			
	142.7 0			
	$J_{CP} = 0.9$	Dh		
	140–125 M	PII		
	62.2 d	CH ₂		
	21.5 S	$CH_3 p$ -tolyl		
	21.4 s			
	16.2 d	CH_3 phos		

 $^{\rm a}\,$ In CD_2Cl_2 at 20 °C, unless otherwise noted.

^b In $CD_3C_6D_5$.

^c In (CD₃)₂CO.

 d At -70 °C.

196.1–195.9 and at 190.7–190.2 ppm due to the carbon resonances of two CO ligands which are magnetically non-equivalent. The values of the two J_{CP} also suggest that each carbonyl is in *cis* position with respect to the two phosphites. In the spectra, the isocyanide carbon resonance also appears as a broad signal at 153.0–141.6 ppm.

On the basis of these data, geometry **I** (Scheme 1) is proposed for monoisocyanide complexes **1** and **2**.

The IR spectra of bis(isocyanide) complexes **3** and **4** show two v_{CN} bands at 2161–2118 cm⁻¹ of the CNR and two v_{CO} absorptions at 1970–1892 cm⁻¹ of the carbonyls, indicating that both the CNR and CO ligands are in a mutually *cis* position. The ¹³C NMR spectra also indicate that both the two CNR and the two CO groups are not magnetically equivalent, in agreement with the presence, in **3a**, of two well separated doublets for both the carbon signals of the isocyanide and carbonyl ligands. The *J*_{CP} values of the two carbonyls are very similar and suggest that both CO are in *cis* position with

respect to phosphites. A geometry of type **II** (Scheme 1) is therefore proposed for bis(isocyanide) complexes **3**, **4**.

3.2. Preparation of trihydridostannyl complexes

Bromo complexes $[ReBr(CO)_2(CNR)L_2]$ (**1**, **2**) and $[ReBr(CO)_2(CNR)_2L]$ (**3**, **4**) react with an excess of $SnCl_2 \cdot 2H_2O$ to give the trichlorostannyl derivatives $[Re(SnCl_3)(CO)_2(CNR)_{3-n}L_n]$ (n = 1, 2) (**5–8**). Treatment of these [M]–SnCl₃ compounds with NaBH₄ in ethanol yielded trihydridostannyl complexes $[Re(SnH_3)(CO)_2(CNR)_{3-n}L_n]$ (n = 1, 2) (**9–12**), which were isolated as white or pale yellow solids and characterised (Scheme 2).

Insertion of SnCl₂ into the Re–Br bond of **1–4** may give the halostannyl intermediate [Re]–SnBrCl₂ which, through halide exchange with SnCl₂, may yield the final trichlorostannyl derivatives [Re (SnCl₃)(CO)₂(CNR)_{3–n}L_n] (**5–8**). However, a metathetic exchange reaction of [ReBr(CO)₂(CNR)_{3–n}L_n] with SnCl₂ to give the chloro



 $R = 4-CH_3OC_6H_4 (5, 7, 9, 11), C(CH_3)_3 (6, 10), 4-CH_3C_6H_4 (8, 12);$ L = P(OEt)₃ (a), PPh(OEt)₂ (b).

Scheme 2.

intermediate [ReCl(CO)₂(CNR)_{3-n}L_n], followed by insertion of SnCl₂ into the Re–Cl bond, may likewise explain the formation of Re–SnCl₃ complexes **5–8**.

Trichlorostannyl complexes [Re]-SnCl₃ (**5–8**) undergo substitution of all three chlorides by H⁻ when NaBH₄ is used as a reagent, thus allowing synthesis of the first trihydridostannyl complexes containing isocyanide as supporting ligand. These results highlight the fact that, in this case too [6a], the introduction of isocyanide ligands in mixed-ligand Re(I) complexes with carbonyls and phosphites allows stabilisation of the tin trihydride group.

The easy synthesis of trihydridostannyl complexes **9–12** by substituting chloride with H⁻ in the metal-bonded SnCl₃ group prompted us to extend the substitution reaction in [Re]–SnCl₃ complexes to other nucleophilic reagents, such as MgBrMe. Results show that the reaction proceeds to give the new trimethylstannyl complex [Re(SnMe₃)(CO)₂(CNC₆H₄-4-CH₃O){PPh(OEt)₂]₂] (**13b**), which was isolated in good yield and characterised (Scheme 3).

The new stannyl complexes **5–13** were isolated as white or yellow solids stable in air and in solution of the most common organic solvents, in which they behave as non-electrolytes [18]. Their formulation is supported by analytical and spectroscopic data (IR and ¹H, ³¹P, ¹³C, ¹¹⁹Sn NMR, Tables 2 and 3) and by X-ray crystal structure determination of complex [Re(SnH₃)(CO)₂{CNC(CH₃)₃}(P-Ph(OEt)₂)₂] (**10b**).



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The IR spectra of trichlorostannyl complexes [Re(SnCl₃)- $(CO)_2(CNR)L_2$ (5, 6) show two v_{CO} bands at 1988–1937 cm⁻¹ indicating the mutually *cis* position of the two CO ligands. One strong band at 2152–2149 cm⁻¹ is also present and attributed to v_{CN} of the isocyanide ligand. The ¹³C NMR spectra confirm the presence of both carbonyl and isocyanide ligands, showing one broad triplet at 147.2-134.9 ppm of the CN carbon atom and two well separated triplets at 194.1-189.6 (5) and 193.4-190.2 (6) ppm of the carbonyl carbon resonance. In addition, the two separated triplets suggest the magnetic inequivalence of the two CO ligands, which are also cis with respect to the two phosphites. At temperatures between +20 and -80 °C, the ³¹P NMR spectra appear as sharp singlets, with the satellites of ¹¹⁹Sn and ¹¹⁷Sn nuclei, matching the magnetical equivalence of the two phosphite ligands. However, the presence of the stannyl ligand is supported by the ¹¹⁹Sn NMR spectra, which show a triplet at -143.0 (**6b**), -144.7 (**5a**) or -141.6 ppm (**5b**) due to coupling with the phosphorus of the two phosphite ligands. On the basis of these data, a cis-trans geometry of type III (Scheme 2) is proposed for trichlorostannyl complexes 5 and 6.

The IR spectra of bis(isocyanide) stannyl complexes [Re(SnCl₃)-(CO)₂(CNR)₂L] (**7**, **8**) indicate that both the two carbonyls and the two isocyanides are in a mutually *cis* position, showing two bands at 1989–1941 cm⁻¹ of the v_{CO} and two bands at 2172–2135 cm⁻¹ of the v_{CN} of the isocyanides. The ¹³C spectra support the presence of both the CO and CNR ligands, showing two well separated doublets at 144.9–140.6 ppm of the carbon resonances of two magnetically non-equivalent isocyanide ligands and two doublets at 190.8–188.2 ppm of the carbon resonances of two magnetically non-equivalent carbonyl ligands. The J_{CP} values of the two carbonyl ligands are very similar (9–11 Hz), suggesting that both CO are in a mutually *cis* position with the phosphite ligand. On the basis of these data, *cis–cis* geometry of type **IV** (Scheme 2) is proposed for stannyl complexes **7** and **8**.

In addition to two v_{CO} bands, characteristic of a *cis* arrangement of the two carbonyl ligands and to one v_{CN} band of the isocyanide, the IR spectra of trihydridestannyl complexes [Re(SnH₃)(CO)₂-(CNR)L₂] (**9**, **10**) show a broad band at 1775–1741 cm⁻¹ (two bands at 1775 and 1744 cm⁻¹ for **9b**) attributed to v_{SnH} of the SnH₃ ligand. Diagnostic for the presence of the tin trihydride as a ligand are the ¹H and ¹¹⁹Sn NMR spectra. In the proton spectra, a triplet at 2.85 (**9a**), 3.5 (**9b**) and 3.33 (**10b**) ppm, with the characteristic satellites due to coupling with ¹¹⁹Sn and ¹¹⁷Sn, was observed and



Fig. 1. Compound $[Re(SnH_3)(CO)_2(CNC(CH_3)_3)(PPh(OEt)_2)_2]$ (10b) drawn at 20% probability level.

attributed to the SnH₃ group. The proton- and phosphorus-coupled ¹¹⁹Sn NMR spectra appear as triplets of quartets at -493.6 (**9a**), -477.0 (**9b**) and -477.3 (**10b**) ppm, due to coupling with the three hydrides and two magnetically equivalent phosphorus nuclei, confirming the presence of the SnH₃ group. At temperatures between +20 and -80 °C, the ³¹P NMR spectra appear as sharp singlets, with the ¹¹⁹Sn and ¹¹⁷Sn satellites, fitting the magnetic equivalence of the two phosphite ligands. Instead, the ¹³C spectra indicate the non-equivalence of the two CO ligands, showing two triplets at 200.0–198.7 and 193.5–193.3 ppm for the carbonyl carbon resonance. On the basis of these data, *cis-trans* geometry of type **IV** (Scheme 2) is proposed for hydridostannyl complexes **9a** and **10b**.

The ORTEP view of complex $[Re(SnH_3)(CO)_2\{CNC(CH_3)_3\}\{P-Ph(OEt)_2\}_2]$ (**10b**) is shown in Fig. 1. A selection of bond lengths and angles are listed in Table 4. The rhenium ion is coordinated by two carbonyl ligands in *cis* positions; two phosphorus atoms of two phosphonite ligands in *trans* positions; a tin atom from a tri-hydridestannyl group; and a carbon atom from a *tert*-butyl isocyanide group. The coordination polyhedron around the rhenium may be defined as a slightly distorted octahedron. Axial angles range from 170.8(5) to 179.2(4) in such a way that both the P–Re–P axis and, especially, the isocyanide–Re–carbonyl axis are bent towards the tin ligand. The *cis* angles range from C(31)–Re–Sn, 83.6(4) to C(1)–Re–C(31), 97.2(5)°, highlighting this distortion.

Both Re–P bond lengths are almost identical – average 2.362(3) Å – which is the same value found for other complexes with phosphite or phosphonite ligands in *trans* positions [6b,19,20]. The substituents on the phosphorus atoms are situated in a pseudo-staggered fashion, with torsion X–P–P–X angles 163.2(8)° (average, X = O or C) (see Fig. 2, in which the phenyl groups were represented as spheres of arbitrary radii).

The Re–C_{carbonyl} bond lengths are 2.010(15) Å in the case of the carbonyl ligand situated *trans* to the tin atom, and 1.936(14) Å for the carbonyl *trans* to a isocyano ligand – being longer [21] than that *trans* to the stannyl ligand (*vide infra*) because of the strong *trans* influence of the SnH₃ ligand [1f,7]. However, it is difficult making comparisons of the *trans* influence of the trihydridestannyl ligand because of the lack of data. There are only four entries [5,6a,7] in the Cambridge Structural Database version 5.29 updates (August 2008) [22] with the trihydridestannyl ligand coordinated to transition metals. The Re–C bond lengths are similar to those found in other dicarbonyldiphosphoniterhenium(I) complexes [19,20].

The Re–Sn bond distance, 2.7543(14) Å, is slightly shorter than that found in similar compounds such as $[Re(SnH_3)(CO)_2-{P(OEt)_3}_3]$, 2.7632(6) Å, and $[Re(SnMe_3)(CO)_2{P(OEt)_3}_3]$, 2.792(1) Å [6a], or other tin–rhenium complexes [6b]. The Sn–H bond lengths, 1.7(1) Å (average) are similar to those found in similar

2.010(15)

2.361(3)

Selected bond lengths (Å) and angles (°) for 10b .				
Re-C(2)	1.936(14)	Re-C(1)		
Re-C(31)	2.056(12)	Re-P(1)		
Re-P(2)	2.363(3)	Re-Sn		
Sn-H(1)	1.70(2)	Sn-H(2)		

T-1-1- 4

Re-P(Z)	2.303(3)	Re-SII	2.7545(14)
Sn-H(1)	1.70(2)	Sn-H(2)	1.71(8)
Sn-H(3)	1.87(10)	C(31)-N(1)	1.154(15)
N(1)-C(32)	1.436(19)		
C(2)-Re-C(1)	91.4(5)	C(2)-Re-C(31)	170.8(5)
C(1)-Re-C(31)	97.2(5)	C(2)-Re-P(1)	92.9(4)
C(1)-Re-P(1)	91.3(4)	C(31)-Re-P(1)	90.0(3)
C(2)-Re-P(2)	89.7(4)	C(1)-Re-P(2)	92.2(4)
C(31)-Re-P(2)	86.9(3)	P(1)-Re-P(2)	175.60(13)
C(2)–Re–Sn	87.7(4)	C(1)-Re-Sn	179.2(4)
C(31)–Re–Sn	83.6(4)	P(1)-Re-Sn	88.70(10)
P(2)–Re–Sn	87.86(10)	N(1)-C(31)-Re	178.7(13)
C(31)–N(1)–C(32)	165.6(16)	C(34)-C(32)-N(1)	109.2(15)
N(1)-C(32)-C(33)	112.1(16)	N(1)-C(32)-C(35)	104.9(18)
Re-C(1)-O(1)	177.6(14)	Re-C(2)-O(2)	175.1(13)



Fig. 2. Compound $[Re(SnH_3)(CO)_2\{CNC(CH_3)_3\}\{PPh(OEt)_2\}_2]$ (**10b**) drawn at 50% probability level. The substituents of the phosphonite groups were not drawn and the methyl carbon atoms of the 'Bu group were drawn as spheres of arbitrary radii for clarity.

compound [6a], $[Re(SnH_3)(CO)_2\{P(OEt)_3\}_3]$, but these values may be misleading, due to the well-known restrictions of X-ray diffractometry for hydrogen atoms in the proximity of heavy metals and the necessary restraints applied to the model.

The Re– $C_{isocyanide}$ bond length is 2.056(12) Å, shorter than that found in other Re(I) complexes with a *tert*-butyl isocyanide ligand



 $[Re] = [Re(CO)_2(CNC_6H_4-4-CH_3O)\{P(OEt)_3\}_2] (14a), [Re(CO)_2(CNC_6H_4-4-CH_3)_2\{P(OEt)_3\}] (15a).$

Scheme 4.





Scheme 6.

trans to a carbonyl group [23–25]. It is known that the C–N–C bond angle at coordinated isonitriles is a structural parameter that can be used to evaluate the extent of π -backbonding [23,26]. Stronger backbonding increases the sp²-character at the isonitrile nitrogen atom leading to a substantial deviation of the C–N–C bond angle from linearity. The N(1)–C(31)–Re is 178.7(13)° but the C(31)– N(1)–C(32) is of 165.6(16)°. This small deviation from linearity suggests that the isonitrile acts mainly as a σ -donor ligands, but some d \rightarrow p π -backbonding should be considered. The C(31)–N(1) bond length, 1.154(15) Å, is also slightly longer than that found in the above complexes, but still consistent with a triple bond between both atoms.

The IR spectra of bis(isocyanide) trihydridostannyl complexes $[Re(SnH_3)(CO)_2(CNR)_2L]$ (11, 12) suggest that both CO and both CNR ligands are in a mutually cis position, owing to the presence of two v_{CO} and two v_{CN} absorptions. In addition, the ¹³C NMR spectra indicate that both carbonyls and isocyanides are not magnetically equivalent, because of the two well separated doublets observed for carbonyl carbon and isocyanide carbon resonances. The comparable values (10 and 11 Hz) of J_{CP} observed for the two carbonyls suggest that they should occupy the same cis position with respect to phosphite ligands. The IR spectra also show the characteristic v_{SnH} bands of the SnH₃ group, whose presence is confirmed by the doublet, with ¹¹⁹Sn and ¹¹⁷Sn satellites, observed at 2.91-2.89 ppm in the proton NMR spectra and attributed to the hydride resonance. The ¹¹⁹Sn NMR spectra appear as quartets of doublets due to coupling with the three hydrides and one phosphite, matching the presence of the SnH₃ ligand. On the basis of these data, *cis-cis* geometry of type VI (Scheme 2) is reasonably proposed for hydridostannyl complexes 11 and 12.

Besides the signals of the phosphite and isocyanide ligands, the ¹H NMR spectrum of the trimethylstannyl complex [Re(SnMe₃) (CO)₂(CNC₆H₄-4-CH₃O){PPh(OEt)₂}₂] (**13b**) shows a singlet at 0.084 ppm, with the ¹¹⁹Sn and ¹¹⁷Sn satellites, attributed to the methyl resonance of the SnMe₃ group. In the ¹³C NMR spectrum, a singlet at -4.53 ppm, correlated in a HMQC experiment with the proton signal at 0.084 ppm, was attributed to the carbon resonance of the SnMe₃ ligand. However, indicating the presence of the SnMe₃ group is the proton- and phosphorus-coupled ¹¹⁹Sn NMR spectrum, which appears as a complicated multiplet. As the ³¹P spectrum is a sharp singlet, the spectrum may be simulated with an A₂MX₉ model (A = ³¹P, M = ¹¹⁹Sn, X = ¹H) with the parameters listed in Section 2. The good fit between calculated and experimental patterns supports the presence of the SnMe₃ ligand.

The IR spectrum of **13b** shows two v_{CO} bands at 1957 and 1902 cm⁻¹ fitting the mutually *cis* position of the two CO ligands. These ligands are not magnetically equivalent, matching the presence of two triplets at 202.8 ($J_{CP} = 11.7 \text{ Hz}$) and 195.0 ppm ($J_{CP} = 9.8 \text{ Hz}$) for the carbon resonance of the CO ligand. On the basis of these data, *cis*-*trans* geometry (Scheme 3) is proposed for the trimethylstannyl complex **13b**.

3.3. Reactions with CO₂

Trihydridestannyl complexes $[\text{Re}(\text{SnH}_3)(\text{CO})_2(\text{CNR})_{3-n}L_n]$ (**9–12**) (*n* = 1, 2) react with carbon dioxide to give white solids characterised as the dinuclear complexes $[Re{Sn(OC(H)=O)_2 (\mu-OH)}(CO)_2(CNR)_{3-n}L_n]_2$ (**14**, **15**) containing an OH-bridging stannyl group (Scheme 4).

The reaction parallels those of the mixed-ligand complexes $[Re(SnH_3)(CO)_nL_{5-n}]$ [6a] with carbonyl and phosphites, and shows that substituting carbonyl ligands with isocyanides in the [Re]-SnH₃ fragment does not change the reactivity of the trihydride group toward CO₂ leading to OH-bridging bis(formate)stannyl complexes **14** and **15**.

In addition, NMR studies on the progress of the reaction of $[Re(SnH_3)(CO)_2(CNC_6H_4-4-CH_3)_2\{P(OEt)_3\}]$ with CO₂ allow us to propose a reaction path of the type shown in Scheme 5, which is very similar to those previously proposed for related [M]-SnH₃ complexes [6a,6c].

The ¹H NMR spectra of the reaction mixture show the disappearance of the multiplet near 2.9 ppm of the SnH₃ group of the precursor and the appearance of resonances attributable to the hydridobis(formate)stannyl intermediate [Re[SnH{OC(H)=O}₂] (CO)₂(CNC₆H₄-4-CH₃)₂{P(OEt)₃}] (**A**).¹ The addition of an equimolar amount of H₂O (by microsyringe) to the reaction mixture containing **A** reveals the direct formation of the dinuclear OH-bridging complex [Re{Sn(OC(H)=O)₂(μ -OH)}(CO)₂(CNC₆H₄-4-CH₃)₂{P(OEt)₃}]₂ (**15a**) and free H₂ [27], according to the path of Scheme 5.

The initial insertion of two CO₂ molecules into two Sn–H bonds of [M]–SnH₃ gives the hydridobis(formate) intermediate **A**, which undergoes hydrolysis with H₂O to yield the final hydroxo-bridging complex **15**. This reaction path also explains why we were not able to isolate the intermediate **A** in pure form, owing to its fast reaction even with the traces of water in common "anhydrous" solvents, to give the final μ -OH derivatives.

Dinuclear complexes **14a** and **15a** were obtained as pale-yellow solids, stable in air and in solution of common organic solvents, where they behave as non-electrolytes [18]. Analytical and spectroscopic data (IR and ¹H, ¹³C, ³¹P and ¹¹⁹Sn NMR, Tables 2 and 3) support the proposed formulation and allow geometry in solution of type **VII** and **VIII** (Scheme 6) to be established.

The IR spectra of monoisocyanide complex **14a** show two v_{CO} bands of two *cis* carbonyl ligands and one band at 2148 cm⁻¹ of the CNR group. Two medium-intensity absorptions at 1673 and 1602 cm⁻¹ are also present due to the v_{OCO} asym band of the two η^1 -formate OC(H)=O groups [28]. The ¹H NMR spectra show, at $-70 \,^{\circ}$ C, the signal of the formate HC= group at 8.31 ppm and the μ -OH resonance at 8.63 ppm. The ¹³C NMR spectra confirm the presence of the formate group showing a singlet at 166.9 ppm of the (H)C=O groups and support the magnetic inequivalence of the two CO groups showing two well separated triplets for the carbonyl carbon atoms. At temperatures between +20 and $-80 \,^{\circ}$ C the signal of the ³¹P NMR spectra is a sharp singlet fitting the magnetic equivalence of the two phosphite ligands. On the basis of these data, *cis-trans* geometry **VII** (Scheme 6) is proposed for **14a**.

The IR spectrum of the bis(isocyanide) complex **15a** suggests that both the two carbonyl and the two isocyanide ligands are in

¹ The ¹H NMR spectra show a singlet at 11.6 ppm, with the ¹¹⁹Sn and ¹¹⁷Sn satellites, attributed to the SnH proton and a singlet at 8.61 ppm of the formate of the intermediate [Re[SnH{OC(H)=O}₂]](CO)₂(CNC₆H₄-4-CH₃)₂[P(OEt)₃]].

a mutually *cis* position. The spectrum also shows the two v_{OCO} asym bands of the tin formate ligands, whose presence is confirmed by the ¹H NMR spectra, showing the HC=O resonance $(-70 \circ C)$ at 8.26 ppm and OH one at 8.61 ppm. The ¹³C spectra support the presence of the tin formate ligand (HC=O signal at 167.0 ppm) and also indicate that the two carbonyl ligands are magnetically non-equivalent owing to the presence of two well separated doublets at 190.4 (J_{CP} = 12.0 Hz) and 189.0 ppm (J_{CP} = 11.3 Hz) for the CO carbon resonances. cis-cis Geometry VIII (Scheme 6) is therefore proposed for dinuclear complex **15a**.

4. Conclusions

In this paper we report the synthesis of mixed-ligand rhenium complexes $[\text{ReBr}(\text{CO})_2(\text{CNR})_{3-n}L_n]$ (*n* = 2, 3) with carbonyl, phosphite and isocyanide, allowing the preparation of unprecedented trihydridestannyl complexes stabilised by isocyanide ligands. Structural parameters for the tert-butyl isocyanide derivative $[Re(SnH_3)(CO)_2\{CNC(CH_3)_3\}\{PPh(OEt)_2\}_2]$ are also reported.

Trimethylstannyl complexes [Re(SnMe₃)(CO)₂(CNC₆H₄-4-CH₃O) {PPh(OEt)₂}₂] and dinuclear tin formate derivatives [Re{Sn(OC(H) =O)₂(μ -OH)}(CO)₂(CNR)_{3-n}L_n]₂ are also described.

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Appendix A. Supplementary material

CCDC 705362 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2009.01.029.

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