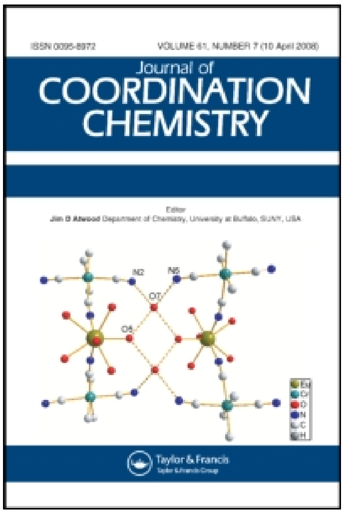

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REACTION OF TRIMETHYLSILYLMETHYLISOCYANIDE WITH MONOMERIC AND DIMERIC RHENIUM COMPLEXES

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Reactions of $CNCH_2SiMe_3$ with several rhenium complexes have been studied. Three new compounds: $Re^{I}Cl(N_2)(CNCH_2SiMe_3)_2(PPh_3)$, $[Re^{III}(CNCH_2SiMe_3)_5Cl_2]BPh_4$ and $Re^{III}Cl_2(CNCH_2SiMe_3)(N_2COPh)(PPh_3)_2$ have been isolated and characterized by IR and ^1H NMR spectroscopies. These results indicate that $CNCH_2SiMe_3$ is less effective than CN^tBu as a ligand.

KEYWORDS: Isocyanide, rhenium, trimethylsilylmethylisocyanide

Alkyl and arylisocyanide complexes of rhenium have been prepared by direct reduction of Re precursors with isocyanide ligands under an inert atmosphere although in a few cases, additional reductants such as $Na_2S_2O_4$ or $SnCl_2$ have been used. The reported mononuclear rhenium(I) and (III) complexes are: $[Re(CNR)_6]^+$, $[ReCl_2(CNR)_5]^+$, $[ReCl_2(CNR)_x(PR_3)_{6-x}]^+$ $(1 < x < 6)$ and $[Re(CNR)_4(PR_3)_2]^+$.[1,6] A few binuclear Re-Re compounds with one or two isocyanide substituents have also been synthesized.[2,3] However, to our knowledge, no rhenium complexes with functionalized isocyanide ligands have been reported. The technetium analogs have been widely developed in relation with radiopharmaceutical applications.

We describe here the reaction of trimethylsilylmethylisocyanide with the monomeric and dimeric Re precursors: $ReOCl_3(PPh_3)_2$, $Re(N_2COPh)Cl_2(PPh_3)_2$, $ReClN_2(dppe)_2$, $Re_2Cl_8[^nBu_4N]_2$ and $Re_2(O_2CCH_3)_4Cl_2$. The CH_2SiMe_3 group (electron attracting and lipophilic) was chosen to study the effect of substituent on the syntheses, solubilities, and stabilities of the corresponding rhenium complexes.

The reactions are summarized in Scheme 1. The complexes have been isolated and characterized by infrared and nuclear magnetic resonance spectroscopies.

EXPERIMENTAL SECTION

All operations were carried out under nitrogen or in a vacuum. Solvents (THF, toluene) were dried over sodium and distilled from sodium-benzophenone under nitrogen. Methanol was distilled over molecular sieves under N_2.

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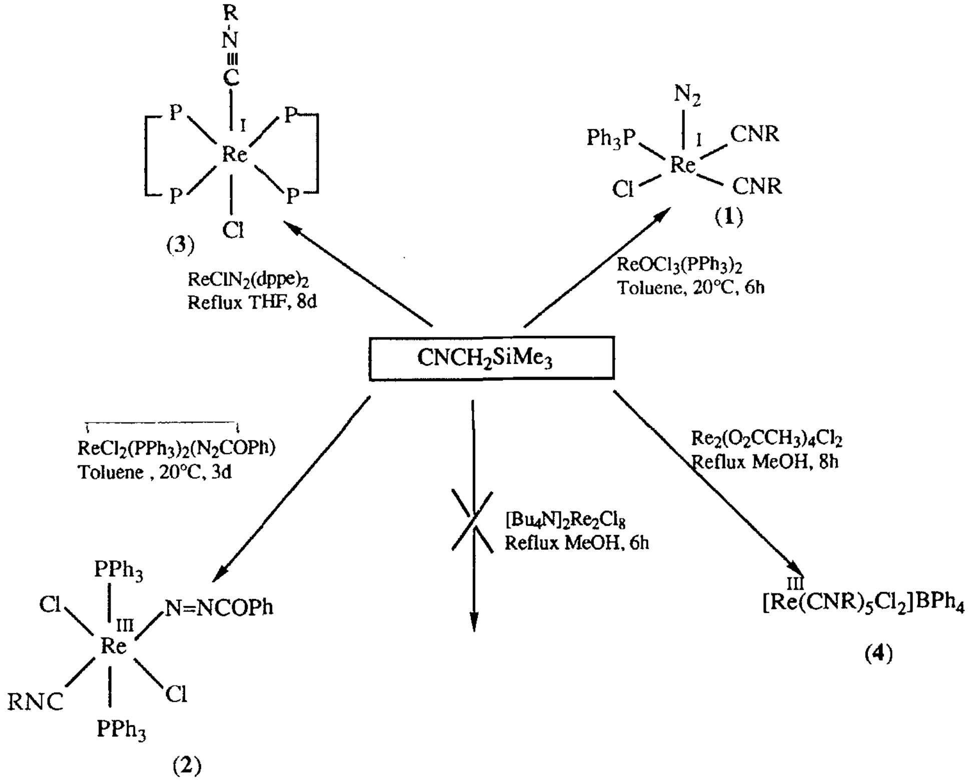


Scheme 1

^1H and ^{31}P NMR spectra were recorded on a Bruker AC 200 with different deuterated solvents: $CDCl_3$, (**1**) and (**3**); CD_2Cl_2, (**2**) and (**4**); IR spectra were recorded as Nujol mulls on a Perkin Elmer 577 and 983 spectrophotometers; the data are in cm^{-1}.

C, H, and N elemental analyses were performed by the service de Microanalyse du Laboratoire de Chimie de Coordination du C.N.R.S, Toulouse, France.

The mononuclear and dinuclear Re complexes are synthesized as described in the literature starting from $KReO_4$ or Re_2O_7 (STREM): $Re^{V}OCl_3(PPh_3)_2$,[4] $ReCl_2(PPh_3)_2(N_2COPh)$,[5] $Re^{I}ClN_2(dppe)_2$,[6] $[^nBu_4N]_2Re_2X_8$,[7] $Re_2(O_2CR_3)_4X_2$.[8]

Syntheses

$CNCH_2SiMe_3$

This ligand has been prepared by improving the procedure of Smith and Livinghouse:[9] 243 ml of BuLi (2.5 M in hexane) were added drop by drop to 25 g (0.61 mol) of CNMe dissolved in 600 ml of dimethoxymethane at −78 °C under stirring. The solution was left 25 min at −78 °C while stirring. The temperature was then lowered to −95 °C and 155 ml of chlorotrimethylsilane was added as fast as possible. The solution was filtered at RT, and the solvent evaporated under vacuum. $CNCH_2SiMe_3$ was purified by distillation under reduced pressure (85°C/80 mmHg).

$ReClN_2PPh_3(CNCH_2SiMe_3)_2$ (1)

To 0.37 g (0.44 mmol) of $ReOCl_3(PPh_3)_2$ suspended in 40 ml of THF was added 1.57 ml (1.25 g; 11.1 mmol) of $CNCH_2SiMe_3$. The resulting mixture was stirred for two days until total dissolution. The solvent was then evaporated under reduced pressure, giving a brown powder which was washed twice with diethylether (20 ml) and dried *in vacuo.* 0.20 g of final product was obtained. The product was recrystallized in a mixture of dichloromethane and ether. (Yield = 62%) *Anal.* Calcd. for $ReClC_{28}H_{37}N_4PSi$(%): C, 45.54; H, 5.05; N, 7.59. Found: C, 45.16; H, 5.32; N, 8.51.

$ReCl_2(PPh_3)_2(CNCH_2SiMe_3)(N_2COPh)$ (2)

To a suspension of 0.5 g (0.55 mmol) of $\overline{ReCl_2(PPh_3)_2(N_2CO}Ph)$ in 50 ml of toluene was added 1.55 ml (1.24 g; 11 mmol) of $CNCH_2SiMe_3$. The mixture was stirred for three days at room temperature. At the beginning of the reaction complete dissolution was observed. Then, precipitation of a light-green powder occurred, which was filtered, washed three times with 20 ml of diethylether and dried *in vacuo.* 0.72 g of (**2**) was obtained. Recrystallization in a mixture of dichloromethane and ether produced (**2**) in 80% yield. *Anal.* Calcd. for $ReCl_2C_{48}H_{46}N_3OP_2Si$(%): C, 56.46; H, 3.86; N, 3.06. Found: C, 56.56; H, 3.76; N, 2.91.

$ReCl(CNCH_2SiMe_3)(dppe)_2$ (3)

To 0.5 g (0.048 mmol) of $ReClN_2(dppe)_2$ suspended in 60 ml of THF was added 0.6 ml (0.48 g; 4.24 mmol) of $CNCH_2SiMe_3$. The mixture was refluxed under argon for 8 days. 30 ml of pentane was added while maintaining the temperature in order to precipitate unreacted $ReClN_2(dppe)_2$. The solution was filtered hot. Evaporation of the solvent produced a powder, which gave unsatisfactory analyses. Despite successive recrystallization attempts in pentane and ether, we were not able to get an analytically pure complex.

$[Re(CNCH_2SiMe_3)_5Cl_2]BPh_4$ (4)

To 0.346 g of $Re_2(O_2CCH_3)_4Cl_2$ suspended in 200 ml of MeOH was added 0.62 ml (0.49 g) of $CNCH_2SiMe_3$. The mixture was refluxed for 10 hours. After evaporation of the methanol under reduced pressure, a saturated solution of $NaBPh_4$ in MeOH (0.23 g of $NaBPh_4$ in 20 ml of MeOH) was added. The solution was stirred for one hour. After evaporation of the solvent, 200 ml of CH_2Cl_2 was added and the excess sodium tetraphenylborate was eliminated by filtration. Concentration of the solution under reduced pressure precipitated a brown powder, which was filtered, washed three times with 20 ml of diethylether and dried *in vacuo.* 0.6 g of (**4**) was obtained (Yield = 52%). *Anal.* Calcd. for $ReBC_{49}Cl_2H_{75}N_5Si$(%): C, 51.51; H, 6.62; N, 6.13; Cl, 6.21. Found: C, 50.10; H, 6.05; N, 6.18; Cl, 5.81.

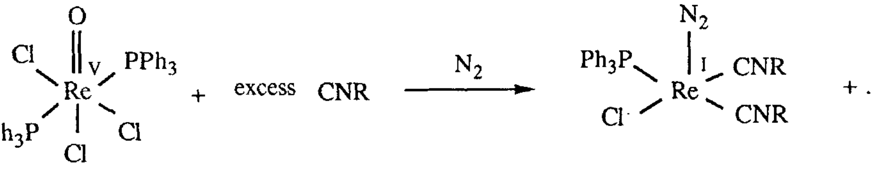
RESULTS AND DISCUSSION

The trimethylsilylmethylisocyanide $CNCH_2SiMe_3$ is a yellow liquid. It polymerizes easily at RT but may be kept indefinitely when stored at -25°C under N_2. Compared to alkyl isocyanides the silyl substituted isocyanide shows the expected decrease in oxidation potential (Ep = 2V in CH_3CN at a glassy carbon electrode).[10] It was interesting to see if this low oxidation potential together with the specific properties of the silyl functional group would influence the reaction of the ligand with rhenium complexes.

Reaction of $CNCH_2SiMe_3$ with Mononuclear Rhenium Complexes

Reaction with $ReOCl_3(PPh_3)_2$

Addition of excess $CNCH_2SiMe_3$ to a suspension of $ReOCl_3(PPh_3)_2$ in toluene, under nitrogen, at room temperature, led after two days to the formation of $Re^ICl(N_2)(CNCH_2SiMe_3)_2(PPh_3)$ (**1**) in 62% yield. (**1**) is air stable and soluble in the major organic solvents except pentane and ether.



(1)

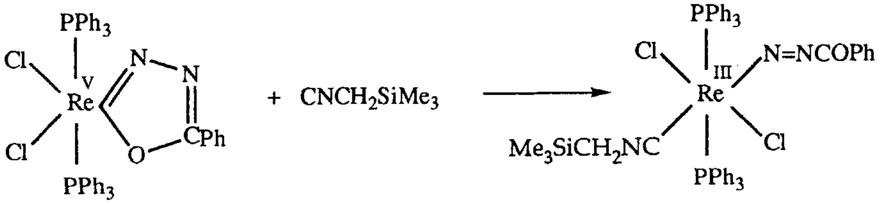
The presence of two *cis*-isocyanide groups is deduced from the ^1H NMR and IR data. The two non equivalent $CNCH_2SiMe_3$ ligands are characterized in the ^1H NMR by two singlets at 0.11 and 0.23 ppm for CH_3 (18H) and at 2.86 and 3.59 ppm for the methylene group (4H). The IR spectrum contains two ν(CN) at 2185 and 2175 cm^{-1} shifted by coordination to higher energy from the free ligand value of 2134 cm^{-1} ($\Delta\nu$ = 51 and 41 cm^{-1} respectively).

The aromatic protons of PPh_3 appear as a multiplet at 7.56 ppm in the ^1H NMR (15H) while the phosphorus resonance is characterized by a singlet at -4.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The presence of coordinated N_2 is deduced from the $\nu(N{\equiv}N)$ stretch at 2100 cm^{-1}, which is in the range where N_2 coordinated end-on to rhenium is observed. The observed reaction is not unexpected since N_2 is well known to stabilize low valent rhenium complexes.[3] In agreement with this is the fact that no complex can be isolated when the reaction is performed under argon. The Re complexes are generally hexacoordinated (*vide infra*). Thus, this five-coordinated species may result from the presence of sterically hindered PPh_3 and $CNCH_2SiMe_3$ ligands, which prevent coordination of another bulky PPh_3 group.

Basic media could not be used because of the presence of the $SiMe_3$ function. Thus the method used to prepare $[Re(CN^tBu)_6]^+$ *i.e.* reaction of $Na_2S_2O_4$ on ReO_4^- in NaOH (pH = 12) cannot be used for $CNCH_2SiMe_3$.

Reaction with $\overline{ReCl_2(PPh_3)_2(N_2CO}Ph)$

Reacting excess $CNCH_2SiMe_3$ with $\overline{ReCl_2(PPh_3)_2(N_2CO}Ph)$ dissolved in toluene, at room temperature, gave the Re^{III} complex (**2**) in good yield. (**2**) is air sensitive and soluble in the major organic solvents except pentane and ether. Only one isocyanide ligand is present in the rhenium coordination sphere in agreement with previous results indicating that only one coordination site is substituted by two electron donor ligands.[11]



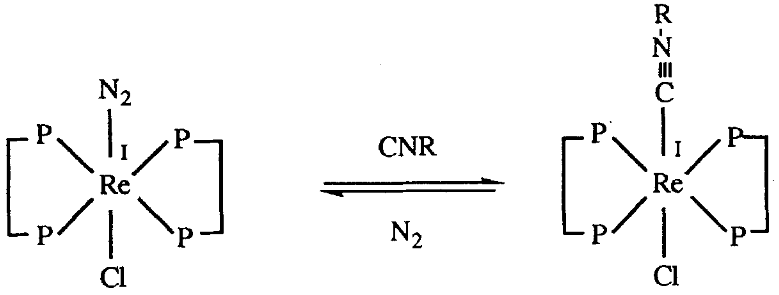
(2)

The structure of (**2**) is demonstrated by $^{31}P\{^1H\}$ NMR. The two *trans* phosphine ligands give only one signal at 3.7 ppm. Only one ν(Re-Cl) at 303 cm^{-1} in the IR spectrum indicates a *trans*-location of the two chloride ligands. Coordination of $CNCH_2SiMe_3$ is deduced from the high energy shift of the $\nu(C{\equiv}N)$ frequency at 2214 cm^{-1}, from the free ligand value at 2134 cm^{-1} ($\Delta\nu = 80\ cm^{-1}$). The $\nu(C{\equiv}N)$ values in (**1**) and (**2**) are in agreement with the rhenium oxidation state data; the less electron rich Re^{III} center (**2**) gives less electron density to the isocyanide ligand through back donation than the Re^I center of (**1**) thus producing a higher energy for the $\nu(C{\equiv}N)$ stretch. The ^1H NMR spectrum shows the two singlets at −0.24 ppm (9H) and at 2.2 ppm (2H) characteristic of the methyl and methylene protons of the CH_2SiMe_3 substituent and the multiplet at 7.57 ppm (35H) corresponding to the phenyl groups.

Reaction with $ReClN_2(dppe)_2$

Reactions of alkyl and aryl isocyanides with this precursor have shown that although N_2 has a great affinity for Re, it can be substituted by CNR when R is CH_3, $C(CH_3)_3$, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 2,6-$Cl_2C_6H_3$. However the process is slow and needs a combination of heating, time and irradiation. The reaction with $CNCH_2SiMe_3$ was not complete even after three weeks of heating at 100°C. A mixture of the monoisocyanide complex (**3**) and of $ReClN_2(dppe)_2$ remained present when the reaction was followed by $^{31}P\{^1H\}$, ^1H NMR and IR spectroscopies. Separation of the two compounds by fractional crystallization was not successful. No improvement in yield was observed when the reaction was performed with a large excess of trimethylsilylmethylisocyanide or when the isocyanide was added i) at the beginning, ii) in the mean time or iii) at the end of the reaction, or if the reaction was run under argon.

The two signals present at 27.4 ppm and 32.2 ppm in the $^{31}P\{^1H\}$ NMR are attributed to $ReClN_2(dppe)_2$ and (**3**) respectively. The ^1H spectrum shows the two singlets at 0.25 ppm (CH_3) and 3.2 ppm (CH_2) of the coordinated $CNCH_2SiMe_3$ and the broad singlet at 2.2 ppm (CH_2) and multiplets at 6.8 and 7.8 ppm corresponding to the protons of the dppe. Similarly, the IR spectrum indicates the



(3)

$\nu(N_2)$ stretches at 1976 and 1944 cm^{-1} for $ReClN_2(dppe)_2$ and the $\nu(C{\equiv}N)$ at 1833 cm^{-1} for (3). This stretching frequency which is shifted to low energies by comparison with the one of free ligand ($\Delta\nu = -301$ cm^{-1}) is in agreement with the values reported for the related CNMe and CN^{t}Bu/Re complexes. The C-N bond character is more double than triple. This results from better back donation $d\pi$-$p\pi$ Re-CNR due to the presence of an electron rich metal center (Re^I, d^6) and an electron releasing chloride anion located *trans* to the CNR group and sharing the same metal d_z2 and d_{xz} orbitals.

Reaction of $CNCH_2SiMe_3$ with Dinuclear Re Complexes

A way to prepare mononuclear Re-isocyanide complexes is by reacting excess isocyanide on $(Bu_4N)_2Re_2X_8$, $Re_2(O_2CCH_3)_4Cl_2$ or $Re_2Cl_6(PEtPh_2)_2$.[2] In all the cases, the reaction is performed by heating the mixture under reflux for four to six hours. For example, reaction of CN^{t}Bu with $[^nBu_4N]_2Re_2X_8$ leads to the formation of the heptacoordinated Re^{III} complex: $[ReX_2(CN^tBu)_5]PF_6$. Synthesis of $[Re(CNR)_6]PF_6$ (R = t-butyl, cyclohexyl) needs addition of excess isocyanide on $Re_2(O_2CCH_3)_4Cl_2$ and reaction of an excess of isocyanide on $Re_2Cl_6(PR_3)_2$ is necessary to get the phosphine substituted species $[Re(CNR)_4(PR_3)_2]^{+\cdot}$

Reactions of $CNCH_2SiMe_3$ with $[^nBu_4N]_2Re_2Cl_8$ under reflux in methanol for four, six or eight hours were unsuccessful. These reactions led to the formation of intractable oils which gave no crystallized complex even when reacted with sodium tetraphenylborate. However, $CNCH_2SiMe_3$ refluxed with $Re_2(O_2CCH_3)_4Cl_2$ in methanol for eight hours produced $[Re(CNCH_2SiMe_3)_5Cl_2]BPh_4$ (**4**) as a dark-brown powder after addition of $NaBPh_4$. (**4**) is air sensitive and soluble in alcohols and dichloromethane.

$$Re_2(O_2CCH_3)_4Cl_2 + \text{excess } CNCH_2SiMe_3 \xrightarrow[-CH_3CO_2Na]{+NaBPh_4} [Re(CNCH_2SiMe_3)_5Cl_2]BPh_4 \quad (4)$$

A conductivity measurement in methanol confirms the existence of a 1/1 electrolyte ($\Lambda = 86.5\ \Omega^{-1}$ cm^2 mole^{-1}).[12] Presence of the isocyanide is deduced from the two $\nu(C{\equiv}N)$ stretches which appear as broad bands at 2088 cm^{-1} and 2043 cm^{-1}, shifted to lower energies compared to the free ligand ($\Delta\nu = -46$ cm^{-1} and -91 cm^{-1}, respectively). The ^1H NMR spectrum shows the characteristic signals of $CNCH_2SiCH_3$ as two broad singlets at 0.23 ppm (45H, CH_3), 3.17 ppm (10H, CH_2). The BPh_4 anion shows multiplets between 6.76 and 7.33 ppm (20H).

CONCLUSION

Scheme 1 indicates the new isocyanide/phosphine compounds which have been synthesized when $CNCH_2SiMe_3$ was reacted with different rhenium complexes. They are stable in air as solids but the solutions must be handled under an inert atmosphere.

A different reactivity towards mononuclear and dinuclear complexes of rhenium is observed for the two isocyanides CN^tBu and $CNCH_2SiMe_3$. For example, CN^tBu reduces $Re_2(O_2CCH_3)_4Cl_2$ to $[Re^I(CN^tBu)_6]^+$ while $CNCH_2SiMe_3$ gives only the Re^{III} complex: $[Re^{III}Cl_2(CNCH_2SiMe_3)_5]^+$. This reaction, which is slow and requires energy (heating between 60 and 90°C), is kinetically controlled and competition between complexation, reduction and polymerization is observed. Since CN^tBu is more resistant to polymerization, the reaction can go to completion; this is not the case for $CNCH_2SiMe_3$. Nevertheless, we have observed room temperature reactions implying that reactions of $CNCH_2SiMe_3$ are more rapid and "cleaner" than for CN^tBu. For example its reaction with $\overline{ReCl_2(PPh_3)_2(N_2CO}Ph)$ is complete although the similar reaction with CN^tBu is not. This emphasizes the releasing effect of the $SiMe_3$ substituent. However, as a whole, $CNCH_2SiMe_3$ is less reactive, resulting from the specificity of the $SiMe_3$ substituent (base sensitive) and to the kinetic properties of the rhenium complexes.

Because of these effects and the base sensitivity of the ligand, we did not succeed in preparing the hexacoordinate cation $[Re(CNR)_6]^+$ with $CNCH_2SiMe_3$.

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