Substitution of labile triflate in [(triphos)Re(CO)$_2$(OTf)]: a new synthetic route to mononuclear and dinuclear Re^{I} complexes

Paola Bergamini,[a] Fabrizia Fabrizi DeBiani,[b] Lorenza Marvelli,*[,a] Nicoletta Mascellani,[a] Maurizio Peruzzini,*[,c] Roberto Rossi*[,a] and Piero Zanello[b]

[a] *Dipartimento di Chimica, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy*
[b] *Dipartimento di Chimica, Università di Siena, Pian dei Mantellini 44, 53100 Siena, Italy*
[c] *Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, ISSECC, CNR, Via J. Nardi 39, 50132 Firenze, Italy*

Received* (*in Montpellier, France*) *21st August 1998, Accepted 6th October 1998

New synthetic routes to the neutral complex [(triphos)Re(CO)$_2$(OTf)] [triphos = MeC(CH$_2$PPh$_2$)$_3$, OTf = $CF_3SO_3^-$] (**3**) are reported. The triflate ligand in **3** is labile and can be easily replaced by different halides and pseudohalides (CN^-, N_3^-, SCN^-, $SeCN^-$, OCN^-) to give new mononuclear octahedral Re^{I} complexes of formula [(triphos)Re(CO)$_2$(X)] (X = Cl^-, Br^-, I^-, CN^-, N_3^-, SCN^-, $SeCN^-$, OCN^-). In some cases, when a double proportion of **3** is treated with the appropriate pseudohalide, rare examples of binuclear Re^{I} complexes featuring a single bridging pseudohalide ligand, [{(triphos)Re(CO)$_2$}$_2$(μ-X)]Y (X = CN^-, N_3^-, SCN^-, $SeCN^-$; Y = OTf, BPh_4^-), have been obtained. All of the new Re^{I} complexes have been characterized by conventional spectroscopic methods and by electrochemical and spectroelectrochemical techniques. Selected examples of regioselective electrophilic alkylations of both halide and pseudohalide ligands are also reported. Noticeably, selective methylation of [(triphos)Re(CO)$_2$(η^1-*X*-XCN)] (X = S, Se) affords the complexes [(triphos)Re(CO)$_2${η^1-*X*-X(Me)(CN)}]OTf, which contain the unprecedented methylsulfocyanate and methylselenocyanate ligands.

The coordinatively unsaturated 16-electron fragment [(triphos)Re(CO)$_2$]$^+$ [triphos = MeC(CH$_2$PPh$_2$)$_3$] is a versatile precursor for a large number of Re^{I} organometallic complexes containing hydride, vinylidene, alkynyl, acyl, alkyne, carbene and carbyne ligands.[1] Removal of a labile ligand disposed *trans* to the triphos apical phosphorus atom is a very simple way to generate this synthon in solution. In this regard, we have already reported that the dihydrogen cationic complex [(triphos)Re(CO)$_2$(η^2-H$_2$)]BPh$_4$ easily eliminates H$_2$ to afford the [(triphos)Re(CO)$_2$]$^+$ moiety.[1] In this paper we show that the easily accessible [(triphos)Re(CO)$_2$(OTf)] (**3**) represents an alternative and more convenient precursor for the generation of the [(triphos)Re(CO)$_2$]$^+$ fragment.

The OTf group has been regarded as a classical "non-co-ordinating" anion for a long time, before the existence of its complexes with different transition metals was definitively proven.[2] Currently, it is considered as a poorly co-ordinating anion and its salts and derivatives are largely used in synthetic inorganic and organometallic chemistry.[2,3] The importance of triflate compounds stems from their many synthetically useful properties such as their good solubility in polar solvents, their lack of oxidizing power, their water stability and, above all, their proclivity to be replaced by many different nucleophiles. This latter property has been related to the electron-withdrawing properties of both the CF_3 and $-SO_2-$ triflate components. The lability of the triflate ligand is of paramount importance for the generation of several co-ordinatively unsaturated species that are largely used for both synthetic and catalytic applications in modern organometallic chemistry.[4]

Complex **3** was previously obtained from the reaction between the neutral monohydride [(triphos)Re(CO)$_2$(H)] (**1**) and MeOTf.[1a] We report now on several improved preparative routes to **3** starting from the more easily available [(triphos)Re(CO)$_2$(Cl)] (**2**). Also, we shall describe the use of **3** as a precursor for the synthesis of a large family of mononuclear and binuclear complexes of Re^{I}. The latter, of formula [{(triphos)Re(CO)$_2$}$_2$(μ-X)]Y (Y = OTf, BPh_4^-), are worthy of mention because they represent unusual examples of bridging symmetrical (X = N_3^-) or asymmetrical (X = CN^-, SCN^-, $SeCN^-$) pseudohalide ligands.

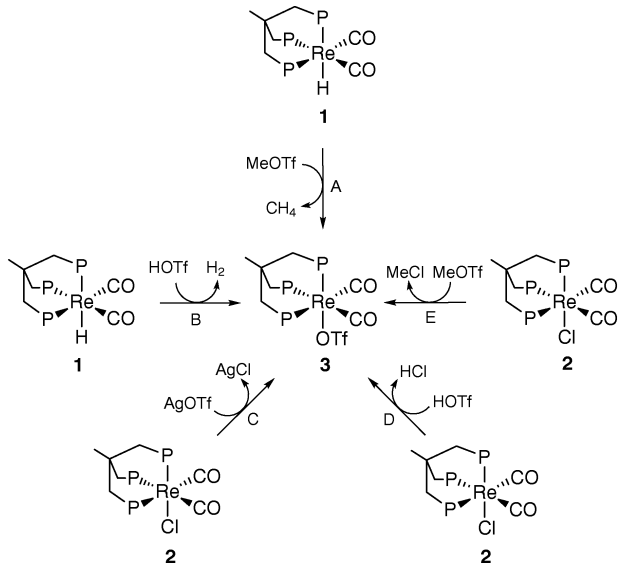
* Corresponding authors' e-mail: Maurizio Peruzzini, peruz@service.area.fi.cnr.it; Lorenza Marvelli, mg1@dns.unife.it

Results and discussion

Synthesis of [(triphos)Re(CO)$_2$(OTf)] (3)

3 represents an important reagent to enter into the chemistry of the very stable Re^{I} fragment [(triphos)Re(CO)$_2$]$^+$, whose organometallic chemistry is currently under examination by our groups.[1] This complex can be prepared by several routes, which are summarized in Scheme 1. The original preparation (route **A**) involves the straightforward alkylation of [(triphos)Re(CO)$_2$(H)] (**1**) with MeOTf, which affords **3** in moderate yield following methane elimination.[1a] The triflate complex **3** can alternatively be synthesized (route **B**) by protonation of **1** with HOTf. This reaction affords **3** upon elimination of molecular hydrogen from the non-classical hydride [(triphos)Re(CO)$_2$(η^2-H$_2$)], which is first formed. Interestingly, although triflate is a very poor co-ordinating ligand and the molecular hydrogen complex is stable at room temperature, co-ordination of triflate ion is competitive even when a protective H$_2$ atmosphere is employed.[5]

In order to avoid the use of the hydride complex and to improve the preparation of **3**, we decided to search for a more simple route starting from the readily accessible [(triphos)Re(CO)$_2$(Cl)] (**2**).[1] In agreement with our expectations, we have found that **3** can be prepared by several alternative strategies, which share the use of **2** as starting material. These synthetic procedures include: the metathesis of chloride by triflate using AgOTf (route **C**), the reaction of **2** with HOTf



Scheme 1

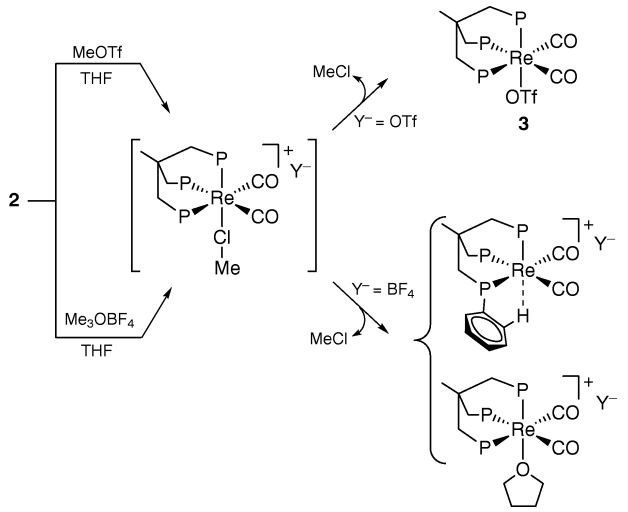
(route **D**) and the electrophilic alkylation of **2** with MeOTf (route **E**).

Method **C** affords **3** by removal of the chloride ligand from **2** in the form of insoluble AgCl. This is a very reliable and sound synthetic procedure (yield higher than 85%), but is not useful for a bulk preparation of **3** due to the use of the light-sensitive and relatively expensive silver triflate.

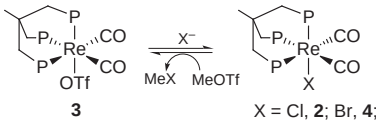
Protonation of **2** with HOTf (method **D**) is an alternative method for the preparation of **3**. From a mechanistic point of view, we hypothesise that **3** is formed following the elimination of a weakly co-ordinated HCl ligand from a transient and undetected adduct of formula $[(triphos)Re(CO)_2(HCl)]^+$. Co-ordination of HCl is well-documented by *in situ* NMR experiments and has been reported to be the first step of the proton transfer reaction on hydride ligands.[6] In the case of the rhenium hydride $[(triphos)Re(CO)_2(H)]$ (**1**), it has been demonstrated by IR and NMR techniques that on protonation of the hydride complex, the formation of a labile hydrogen-bond adduct takes place before the hydrogen transfer step is completed.[7]

Nevertheless, the formation of HCl as a secondary product of route **D** may cause several complications in the isolation of **3** as well as in its use in further chemical reactions. Thus, the remaining procedure E, which falls under the same reaction paradigm, appears as the most convenient to prepare **3** because the only secondary product that is formed is the volatile and easily removed MeCl. The reaction occurs promptly (5 min), providing an easy access to pure **3** in high yield (90%). The elimination of MeCl from **2** is the key step in the formation of **3**, as confirmed by an *in situ* ^1H NMR experiment ($CDCl_3$), which features a singlet at 3.0 ppm ascribable to CH_3Cl.

Although electrophilic alkylation of halide complexes has been scarcely considered from a synthetic point of view, there are some precedents indicating that a halide ligand can be removed in the form of the corresponding halogenated hydrocarbon upon reaction with methyl triflate.[8] In the case at hand, addition of MeOTf likely forms an unstable $[(triphos)Re(CO)_2(ClMe)]^+$ cation (Scheme 2) in which MeCl acts as an η^1-ligand towards the rhenium centre by using a lone pair on the chloride atom. In keeping with this hypothesis, it is worthy of mention that an extensive literature exists on the co-ordinating abilities of several halocarbons toward strong Lewis acid moieties,[9] including some rhenium assemblies.[10] The chloromethyl compound, however, has not been intercepted, even when the alkylation reaction is carried out at low temperature in an NMR tube and it is monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Probably, the intrinsic instability of the halocarbon adduct is due to the existence of easy reactivity paths that eliminate MeCl. Thus, MeCl is readily substituted by the triflate counter anion to give **3**. Even in the absence of co-ordinating anions, the halocarbon adduct is replaced in the co-ordination sphere of the metal by an intramolecular agostic interaction, or, depending on the nucleophilicity of the solvent, by solvent co-ordination. As a matter of fact, on repeating the electrophilic attack on **2** with the Meerwin reagent, Me_3OBF_4, in THF, the agostic derivative $[(triphos)Re(CO)_2]BF_4$ is the principal species formed, together with some $[(triphos)Re(CO)_2(\eta^1\text{-}OC_4H_8)]^+$.[11]



Scheme 2



Scheme 3

Substitution reactions of [(triphos)Re(CO)$_2$(OTf)] with X$^-$ [X = Cl, (2); Br, (4); I, (5)]

When a THF solution of $[(triphos)Re(CO)_2(OTf)]$ is stirred with the halide salts NaCl, KBr or KI at room temperature, the mononuclear complexes $[(triphos)Re(CO)_2(X)]$ [X = Cl, (**2**); Br, (**4**); I, (**5**)] are obtained after a few hours stirring (Scheme 3). All of these complexes are air-stable in both the solid state and solution. They are sparingly soluble in dichloromethane and chloroform and behave as non-electrolytes in nitroethane.

Attempts to prepare the corresponding fluoroderivative by the same route, using different sources of fluoride such as NaF, KF or (PPN)F, were unsuccessful, most likely because of the low affinity of the very hard base fluoride for the soft Re^I acid.[12,13]

The bromo and iodo derivatives, **4** and **5**, react with an excess of methyl triflate to reform $[(triphos)Re(CO)_2(OTf)]$. As anticipated above for the reaction of **2** with MeOTf, elimination of CH_3Br or CH_3I was observed, respectively, by ^1H NMR spectroscopy.[8] Complexes **4** and **5** have been characterized by elemental analysis, IR and multinuclear NMR spectroscopies (Table 1) as well as by electrochemical measurements (see below, Table 2). The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** exhibit the AM_2 splitting pattern expected for an octahedral complex with the tripodal triphos ligand occupying a face of the co-ordination polyhedron.[14–16]

Synthesis of [(triphos)Re(CO)$_2$(CN)] (6) and [{(triphos)Re(CO)$_2$}$_2$(μ-CN)]OTf (7)

When the triflate complex **3** is treated with 5 equiv. of $[Bu_4N]CN$ in THF at room temperature, yellow micro-

Table 1 $^{31}P\{^1H\}$ NMR spectral data and selected IR spectral absorptions for the complexes[a]

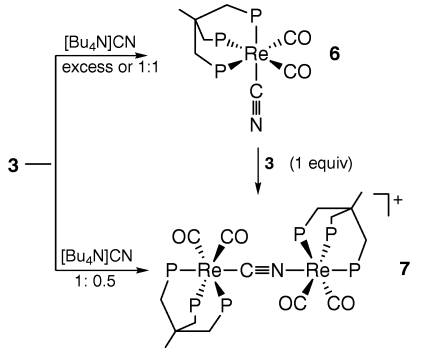
Complex	$^{31}P\{^1H\}$			IR	
	δ_A/ppm	δ_M/ppm	J_{AM}/Hz	$\nu_{(CO)}$/cm^{-1}	$\nu_{(other)}$/cm^{-1}
3	6.20	−10.11	14.7	1967, 1902	1320 ν(η^1-OTf)
2	2.40	−18.23	14.7	1948, 1887	
4	2.15	−20.14	14.6	1950, 1889	
5	−0.12	−24.70	15.3	1950, 1892	
6	−5.90	−17.88	18.4	1946, 1890	2106 ν(CN)
7[b]	0.21, −7.41	−17.12, −17.66	16.3, 19.5	1967, 1908	2097 ν(CN), 1275 ν(OTf)
8	1.07	−15.07	14.9	1936, 1879	2044 $\nu_{as}(N_3)$, 1334 $\nu_{sy}(N_3)$
9	0.75	−11.96	16.3	1952, 1894	2122 $\nu_{as}(N_3)$, 1272 ν(OTf)
10	−2.42	−15.95	17.0	1956, 1900	2106 ν(SCN)
10′	0.07	−15.58	17.1		2077 ν(NCS)
11	−3.41	−16.18	17.4	1958, 1898	2103 ν(SeCN)
11′	−0.23	−15.01	16.0		2066 ν(NCSe)
12[b]	−2.13, −2.52	−12.90, −14.70	18.3	1958, 1900	2140, ν(SCN), 1273 ν(OTf)
13[b]	−2.18, −3.47	−12.90, −15.97	18.1	1960, 1900	2142 ν(SeCN), 1271 ν(OTf)
14/14′[b]	1.79, 3.75	−16.42, −18.94	15.3, 13.7	1950, 1886	2234 ν(NCO)
15	−12.04	−14.15	21.5	1971, 1915	2184 ν(CN), 1269 ν(OTf)
16	−5.19	−10.52	19.2	1956, 1900	2139 ν(SCN), 1267 ν(OTf)
17	−4.60	−9.93	19.6	1956, 1898	2183, ν(SeCN), 1271 ν(OTf)
18	−3.53	−13.10	18.2		

[a] The $^{31}P\{^1H\}$ NMR spectra were recorded in CD_2Cl_2 at room temperature and all exhibit an AM_2 splitting pattern. [b] $(AA'M_2M'_2)$ spin systems.

crystals of the cyanide complex **6**, [(triphos)Re(CO)$_2$(CN)], are obtained in pure form and good yield (Scheme 4). Complex **6** is a non-electrolyte in nitroethane and exhibits an IR spectrum featuring, besides the two strong carbonyl stretching vibrations, a very strong band (2106 cm^{-1}) assigned to ν(CN)[17] (Table 1).

The high-energy shift of the cyanide absorption with respect to unco-ordinated cyanide (2050 cm^{-1} in [Bu$_4$N]CN) points to a stronger σ-donor than π-acceptor contribution in the Re—CN bond.[17,18] This behaviour, which has been already reported by Gladysz and coworkers for the mononuclear [Cp*Re(NO)(PPh$_3$)(CN)] (Cp* = C$_5$H$_5$ or C$_5$Me$_5$) comp lexes,[10c,19] suggests an increase of the M dπ → CO π* back-donation and agrees also with the low-frequency shift observed for the CO stretches (1946, 1890 cm^{-1}), in comparison to the triflate complex **3** (1967, 1902 cm^{-1}). The cyanide ligand in **6** exhibits a diagnostic $^{13}C\{^1H\}$ NMR absorption at 131.4 ppm and is coupled to only one phosphorus atom ($^2J_{CP\ trans}$ = 10.9 Hz). Similar NMR parameters have been reported for other mononuclear Re^I-cyanide complexes.[10c, 19a]

Cyanide complexes of transition metals have attracted renewed interest during the last decade because the residual electron density on the nitrogen makes these complexes suitable for use as reagents with electrophilic transition metal fragments, with which they form homo- or heteronuclear bimetallic species in which a cyanide ligand bridges two transition metals.[19b,20] These binuclear compounds appear relevant in the topical areas of material sciences (materials with non-linear optical properties,[21] energy storage devices[22]), as well as biological sciences.[23]



Scheme 4

In order to explore this possibility, we have reacted **6** with a second equivalent of **3**. As a result, the bridging cyanide derivative [{(triphos)Re(CO)$_2$}$_2$(μ-CN)]OTf, (**7**), is obtained in almost quantitative yield. The same product can be prepared by reacting **3** and [Bu$_4$N]CN in a rigorous 1 : 0.5 ratio (Scheme 4).

In keeping with the cationic nature of **7**, the infrared spectrum exhibits a slightly red-shifted CN stretching vibration (2097 cm^{-1}) in comparison to the corresponding band of the neutral monomeric derivative **6** (2106 cm^{-1}),[19b] while the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 consists of two well-separated 1 : 1 AM_2 spin systems, which are temperature invariant in the temperature window of dichloromethane. The NMR pattern reflects the inequivalency of the two donor ends of the cyanide bridge and the different electronic density experienced by the two rhenium atoms. The first set of resonances features a triplet at 0.21 ppm and a doublet at −17.12 ppm ($^2J_{PP}$ = 16.3 Hz), while the second one falls at −7.41 (t) and −17.66 (d) ($^2J_{PP}$ = 19.5 Hz). As a consequence of the different nature of the donor atoms of the CN group, the two axial phosphorus atoms in [(triphos)Re]$^+$ have very different chemical shifts, one being *trans* to carbon and the other one *trans* to nitrogen in the linear P—Re—C≡N—Re—P six atom assembly. Interestingly, one of the two triplets (δ − 7.41) appears much broader than the other one resonating at δ 0.21 and exhibits a significantly longer relaxation time (2.0 *vs.* 0.7 s). This experimental finding allows one to assign the broader resonance to the P atom located *trans* to the nitrogen end of the cyanide ligand. It is indeed conceivable that the strong interaction with the ^{14}N nucleus, which has a large electric quadrupolar moment, causes severe line broadening of the phosphorus resonance. Moreover, the concomitant increase of T_1 measured for the same P resonance presumably reflects the smaller magnetic moment of ^{14}N *vs.* ^{13}C, which, reducing the dipolar–dipolar interaction, increases the relaxation time of the faced P nucleus.[24,25]

Synthesis of [(triphos)Re(CO)$_2$(N$_3$)] (8) and [{(triphos)Re(CO)$_2$}$_2$(μ-N$_3$)]Y [Y = OTf, (9); BPh$_4^-$, (9-BPh$_4$)]

When a large excess (≥3 equiv.) of bis(triphenylphosphoranylidene)azide is added to a stirred dichloromethane solution of **3**, the yellow colour immediately turns deep red. Addition of *n*-hexane precipitated pale yellow microcrystals of

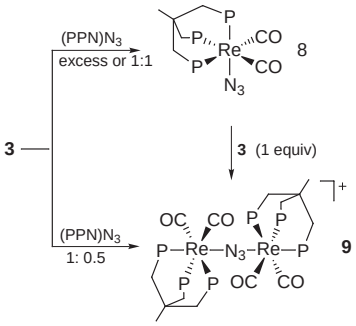
[(triphos)Re(CO)$_2$(N$_3$)] (**8**), in good yield (Scheme 5). **8** behaves as a non-electrolyte in dichloromethane and exhibits in the IR spectrum two strong bands at 2044 and 1334 cm^{-1}, which are assigned to the antisymmetric and symmetric stretches of a terminal azido ligand, respectively.[18,26]

Monitoring in THF the reaction of **3** with a stoichiometric amount of (PPN)N$_3$ by ^{31}P{^{1}H} NMR, a second less intense AM$_2$ spin system is observed together with the resonances of **8**. The two products are formed in a 10 : 1 ratio, which does not change within a week and does not appear to be temperature dependent. The new product can be obtained in pure form and quantitative yield by allowing **3** to react with (PPN)N$_3$ in a rigorous 1 to 0.5 ratio. On the basis of several observations, the binuclear formula [{(triphos)Re(CO)$_2$}$_2$(μ-N$_3$)]OTf, in which an azido ligand is sandwiched between two symmetric [(triphos)Re]$^+$ moieties, is assigned to **9**. In particular, the IR spectrum shows a strong and broad absorption at 2122 cm^{-1}, characteristic of bridging azido ligands.[26]

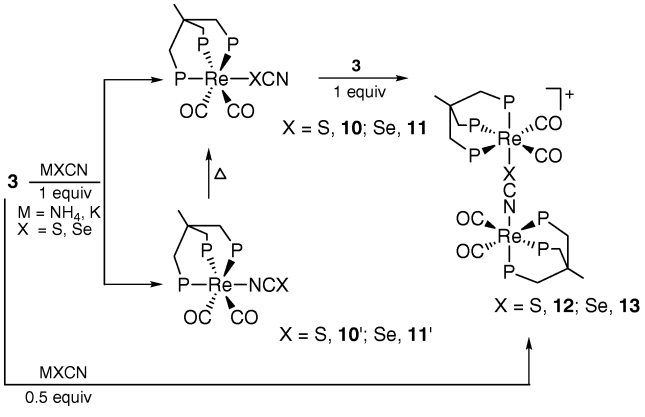
Terminal azido complexes of the transition metals have been reported to undergo thermal N$_2$ elimination to afford metal-nitride complexes.[27] In particular, this reaction readily takes place with rhenium derivatives in high oxidation states of the metal, owing to the high stability of the Re≡N core.[28] In the present case, however, no reaction occurs even under forcing conditions and the starting mono- and binuclear azido complexes are recovered unchanged after prolonged reflux in THF.

Synthesis of the pseudohalide complexes [(triphos)Re(CO)$_2$(η^1-*X*-XCN)] [X = S, (10); Se, (11)] and [{(triphos)Re(CO)$_2$}$_2$(μ-η^1-*X*, η^1-*N*-XCN)]OTf [X = S, (12); Se, (13)]

Addition of a large excess of NH$_4$SCN to a stirred THF solution of **3** at room temperature results in the formation of the purple neutral complex [(triphos)Re(CO)$_2$(η^1-*S*-SCN)] (**10**), where the thiocyanate ligand is *S*-co-ordinated to rhenium, (Scheme 6). Thiocyanate (and selenocyanate, see below) complexes exhibit linkage isomerism, being capable of co-ordinating the metal using either the nitrogen end or the terminal chalcogen donor atom.[29,30]



Scheme 5



Scheme 6

A useful and largely applied diagnostic tool, to discriminate between the two possible linkage isomers, is IR spectroscopy. In this respect, a useful marker for assigning the *N*-bound *vs.* *X*-bound co-ordination is the ν(CN) band above 2000 cm^{-1}.[18,29b,31] In the thiocyanate complex **10**, the presence of an *S*-co-ordinated ligand is readily inferred from the strong ν(CN) band at 2106 cm^{-1}. This absorption is moved to a higher frequency with respect to the unco-ordinated thiocyanate anion, suggesting that the ligand is *S*- rather than *N*-bound.[29b,31] This behaviour markedly differs from that reported by Abram and co-workers for the Re^{V} and Re^{III} compounds of formula [ReN(NCS)$_2$(CH$_3$CN)(Ph$_3$P)$_2$], [ReN(NCS)$_2$(Me$_2$PhP)$_3$], [Re(NS)(NCS)$_2$(Me$_2$PhP)$_3$] and [ReCl$_2$(NCS)(Me$_2$PhP)$_3$], for which an *N*-co-ordination has been proposed by IR measurements and has been authenticated by X-ray diffraction analysis.[32]

In the case at hand, a rationale for the preference of *S*-co-ordination *vs.* *N*-co-ordination may be found in the softness of Re^{I}, which therefore exhibits a higher affinity for sulfur than for nitrogen. In keeping with the presence of an *S*-bound thiocyanate ligand in **10**, the ^{13}C{^{1}H} NMR spectrum exhibits a broad singlet at 124.5 ppm, which is in line with other NMR authenticated *S*-bound thiocyanates.[33]

On replacing NH$_4$SCN with KSeCN in the previous reaction, deep green microcrystals of [(triphos)Re(CO)$_2$(η^1-*Se*-SeCN)] (**11**) are obtained in good yield. On the basis of similar arguments [ν(CN) at 2103 cm^{-1} and an upfield-shifted quartet in the ^{13}C{^{1}H} NMR spectrum at δ 108.9 [33]] the presence of a Se-bound selenocyanate ligand is hypothesized in complex **11**. This structural assignment is indirectly supported by an *in situ* NMR study of the alkylation reaction with MeOTf (see below), which points to the occurrence of a regioselective methylation of the selenium atom.

Monitoring the reaction between **3** and one equivalent of NH$_4$SCN in THF-d$_8$ (in a 5 mm NMR tube by ^{31}P{^{1}H} NMR spectroscopy) reveals that the AM$_2$ pattern attributed to **10** (*ca.* 70%) (δ$_A$ − 2.42, δ$_M$ − 15.95, J_{AM} 17.0 Hz) is flanked (*ca.* 20%) by a second AM$_2$ spin system (**10′**) with similar chemical shifts and coupling constants (δ$_A$ 0.07, δ$_M$ − 15.58, J_{AM} 17.1 Hz). On heating a sample of this mixture at 60 °C for 3 days **10′** transforms completely and irreversibly in **10**. A slower transformation converting **10′** into **10** takes place also at room temperature. Although a definitive structural assignment of this minor component is not possible on the basis of the ^{31}P{^{1}H} NMR data only, we hypothesize that it corresponds to the *N*-bound isomer [(triphos)Re(CO)$_2$(η^1-*N*-NCS)], (**10′**), which is formed together with **10** when **3** is reacted with ammonium thiocyanate. On increasing the temperature or even on prolonged standing at room temperature, **10′** transforms into the more stable isomer **10**. Opposite conversion (from the *S*-bound to the *N*-bound isomer) has also been reported.[33]

A similar behaviour is observed when studying the reaction of **3** with KSeCN, which at room temperature gives a mixture of two octahedral complexes, [(triphos)Re(CO)$_2$(η^1-*Se*-SeCN)] (**11**) and [(triphos)Re(CO)$_2$(η^1-*N*-NCSe)] (**11′**), in an approximate 1 : 1 ratio. On standing at room temperature, the transformation of **11′** in **11** is faster than the analogous transformation of **10′** into **10**. At reflux temperature in THF, the isomerization of **11′** into **11** occurs within 1 d.

During the analysis of the ^{31}P{^{1}H} NMR experiments with NH$_4$SCN (or KSeCN), a new complex **12** (or **13**) featuring two AM$_2$ sets of equal intensity appears in the spectrum (⩽10%) together with the isomeric mixture of **10** and **10′** (or **11** and **11′**). Noticeably, these minor components do not transform into any of the isomeric products after prolonged standing at room temperature or after 3 days heating to 60 °C. In contrast, addition of a second equivalent of **3** to a solution of **10** and **10′** (or **11** and **11′**) readily converts this mixture into **12** (or **13**), which becomes the only rhenium-containing product.

Thus, we attribute to **12** and **13** the dinuclear formula [{(triphos)Re(CO)$_2$}$_2$(μ-η^1-*X*,η^1-*N*-XCN)]OTf (X = S, **12**; Se, **13**). Compounds **12** and **13** may be quantitatively prepared by reacting **3** with half an equivalent of the appropriate thio- or selenocyanate. Their IR spectra show the typical bands of the bridging chalcogenocyanate ligands at 2140 (**12**) and 2142 (**13**) cm^{-1}.[29b]

Reaction of 3 with NaOCN

On replacing the thio- or selenocyanate salt with sodium cyanate in the above procedure a 7 : 3 mixture of the two linkage isomers, [(triphos)Re(CO)$_2$(η^1-*N*-NCO)] (**14**) and [(triphos)Re(CO)$_2$(η^1-*O*-OCN)] (**14′**) is obtained. No attempts were made to separate the two isomers. The formation of two mononuclear cyanate complexes was inferred by IR and NMR spectroscopy[29b] (see Table 1). However, we were unable to assign the different signals to each of the two isomers. Noticeably, no evidence for the formation of dinuclear compounds was obtained by monitoring (^{31}P NMR spectroscopy) the reaction between **3** and NaCNO, even when different ratios of the reagents were used.

Electrophilic alkylation of the pseudohalide complexes with MeOTf

Terminal pseudohalide ligands like cyanide, cyanate and chalcogenocyanate complexes exhibit a residual electron density on the exposed nitrogen and are potentially capable of reacting with different electrophiles to produce the corresponding isocyanide, isocyanate or isochalcogenocyanate metal complexes, respectively. Such a reaction is well-documented for terminal cyanide complexes, which, upon electrophilic attack on the nitrogen end, give metal-stabilized alkylisocyanide ligands.[34] In contrast, this reactivity has been scarcely considered for the cognate cyanate and chalcogenocyanate complexes, which would transform into the elusive isocyanate or isochalcogenocyanate metal complexes. On the other hand, the electrophilic attack could occur also on the rhenium-coordinated sulfur or selenium atom to yield an *S*- or *Se*-bound alkylcyanide species.

Thus, we decided briefly to investigate the electrophilic methylation of the cyanide complex **6** and to extend these studies to the related chalcogenocyanate and cyanate complexes **10**, **11** and **14/14′**, respectively. Compound **6** reacts with a slight excess of MeOTf to give air-stable yellow microcrystals of [(triphos)Re(CO)$_2$(CNCH$_3$)]OTf (**15**), (Scheme 7). The IR spectrum contains a medium intensity absorption at 2184 cm^{-1} in the region expected for metal isonitriles. The ^{31}P and ^{1}H NMR spectra are consistent with the presence of the methyl isocyanide complex. Particularly, the proton NMR spectrum contains a singlet at 3.06 ppm assigned to the three protons of the methyl isocyanide ligand.

A different regioselectivity takes place with repeating the same reaction with the thiocyanate complex **10** and the selenocyanate derivative **11**. After addition of MeOTf and usual work-up, orange to pale yellow microcrystals of the new methylchalcogenocyanate complexes [(triphos)Re(CO)$_2${η^1-*S*-S(Me)(CN)}](OTf (**16**) and [(triphos)Re(CO)$_2${η^1-*Se*-Se(Me)(CN)}]OTf (**17**) are obtained in very good yields, (Scheme 7). Compounds **16** and **17** are air-stable in the solid state and do not decompose in solutions of chlorocarbons within a week. The existence of an η^1-*S*- or η^1-*Se*-co-ordinated S(Me)(CN) or Se(Me)(CN) ligand in **16** and **17**, respectively, was confirmed by the observation in the ^{1}H NMR spectrum of **17** of a couple of broad selenium satellites flanking the methyl resonance at 2.28 ppm (Fig. 1). The magnitude of the $^2J_{HSe}$ coupling constant (13.1 Hz), which is in the range reported for organic selenide complexes,[35] is clear-cut proof for the occurrence of the regioselective alkylation of the chalcogen rather than the nitrogen atom of the chalcogenocyanate ligand. A similar regioselectivity is assigned to the sulfur derivative **16** on the basis of the very similar NMR and IR properties.

When the selenocyanate complex **11** is treated with MeOTf at low temperature [^{31}P{^{1}H} NMR spectroscopy (−30 °C)] two different products (**17**, 70%; **18**, 30%) are formed, (Scheme 8). Heating the sample at room temperature converts the minor product **18** into **17**, which, within one hour, becomes the only detectable rhenium phosphine complex. This observation indicates that at low temperature the reaction is kinetically controlled and there is no selectivity in driving the

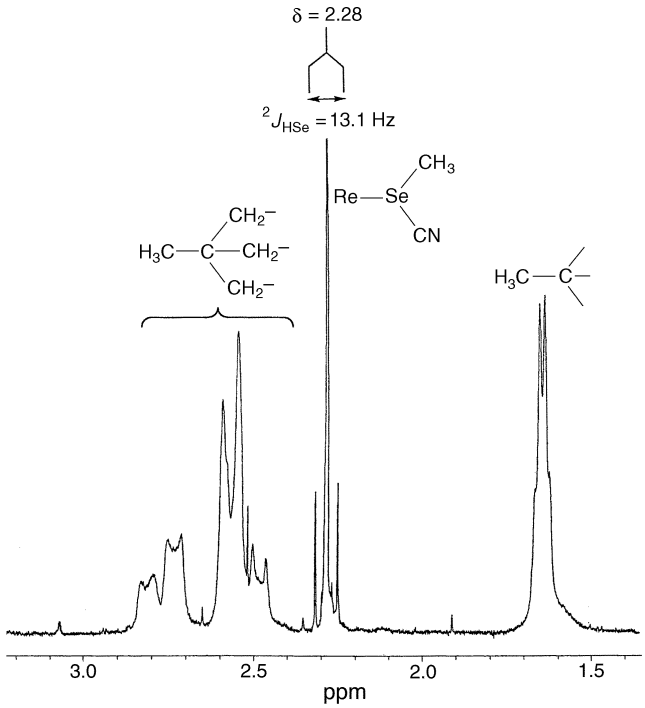
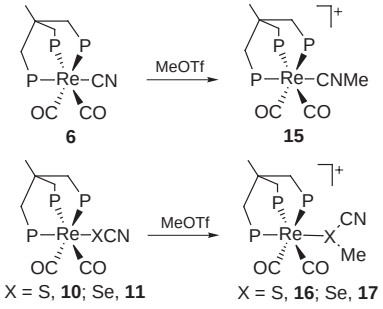
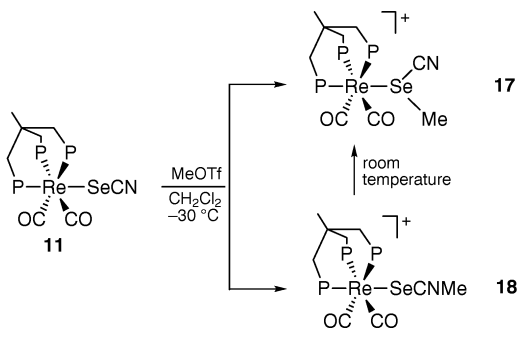


Fig. 1 ^{1}H NMR (200.13 MHz, CD_2Cl_2, 25 °C, TMS reference) spectrum of **17** in the aliphatic region showing the $SeCH_3$ resonance with the satellites due to H–^{77}Se coupling.



Scheme 7



Scheme 8

electrophilic attack, which then proceeds on both the selenium and the nitrogen ends. As a result the two isomers, **17** and the isomethylselenocyanate complex [(triphos)Re(CO)$_2$(η^1-*Se*-SeCNMe)]OTf (**18**), are formed. On increasing the temperature, the reaction becomes thermodynamically controlled and the less favoured isomer **18** is completely transformed into the methylselenocyanate complex **17**, which is indefinitely stable at room temperature in dichloromethane solution. Noticeably, on lowering the temperature down to $-30\,^{\circ}C$, the equilibrium is not restored, thus indicating the irreversibility of the transformation of **18** into **17**.

We have attempted also to study the alkylation reaction of the azide complex **8** as well as of the mixture of the cyanate and isocyanate complexes **14** and **14′**. However, the only product that has been recovered from these reactions is the triflate complex **3**.

Electrochemical properties

All of the monomeric compounds **1**, **2**, **4**, **5**, **8**–**11** and **14** show a single oxidation process (see Table 2) in the range 0.59–0.80 V generally reversible on the CV timescale, with the noticeable exception of [(triphos)Re(CO)$_2$(H)]. Controlled potential coulometry proves the monoelectronic nature of such redox changes. This is ascribable to the Re^{II}/Re^{I} couple and is followed always by chemical complications. No evidence has been found for the presence of the Re^{I}/Re^{0} and the Re^{III}/Re^{II} couples, this last being possibly covered by the irreversible oxidation of the ancillary triphos ligand (1.5 V).

Halide complexes and the hydride analogue. Fig. 2 shows the cyclic voltammogramms in dichloromethane (0.2 M NBu_4PF_6) of [(triphos)Re(CO)$_2$(H)] and [(triphos)Re(CO)$_2$-(Cl)]. The latter is typical for the general behaviour of the halide compounds.

The rhenium hydride complex, [(triphos)Re(CO)$_2$(H)], undergoes an irreversible oxidation process at $E = +0.60$ V, followed by chemical reactions that give rise to a new reversible redox system ($E^{\circ\prime} = +0.69$ V). Scan rates as high as 5000 mV s^{-1} are necessary to prevent the formation of this new species and to observe the directly associated cathodic response [(triphos)Re(CO)$_2$(H)]$^+$ → [(triphos)Re(CO)$_2$(H)]. On the contrary, for compounds **2**, **4** and **5** the same anodic process is both electrochemically and chemically reversible on the CV timescale, as demonstrated by the constant value of $i_{pc}/i_{pa} \approx 1$ as well as by the linear plot of i_{pa} *vs.* the square root of the scan rate. Nevertheless, exhaustive oxidation ($E_w = +1$ V) reveals that the electrogenerated Re^{II} cation complexes, [(triphos)Re(CO)$_2$(X)]$^+$, are unstable and undergo a chemical rearrangement resulting in new redox systems featuring electrochemical reversibility. In the case of **2** and **4**, the potential of the electrogenerated species is anodically shifted ($E^{\circ\prime} = +0.77$ V *vs.* $E^{\circ\prime} = +0.75$ V for **2** and $E^{\circ\prime} = +0.80$ V *vs.* $E^{\circ\prime} = +0.73$ V for **4**).

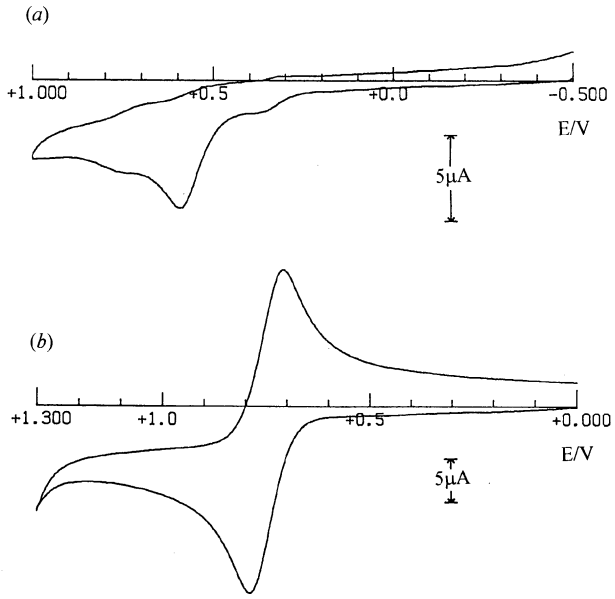


Fig. 2 Cyclic voltammogram of (*a*) a 4.6×10^{-4} M solution of **1** and (*b*) a 10.8×10^{-4} M solution of **2** in CH_2Cl_2–0.2 M NBu_4PF_6. Scan rate 0.2 V s^{-1}.

IR spectroscopy monitoring (see Table 2) of the electrochemical process allows us to examine the products formed upon oxidation of the Re^{I} complexes, following the progressive disappearance of the original ν(CO) bands associated with the appearance of a new unique higher energy band (at 2140 cm^{-1} for **2** and at 2030 cm^{-1} for **4**).[36] In contrast, the new redox system that appears upon exhaustive oxidation of **5** is cathodically shifted ($E^{\circ\prime} = +0.51$ V *vs.* $E^{\circ\prime} = +0.67$ V). In all cases the colourless solutions turn deep violet, this being an almost general feature accompanying the exhaustive oxidation of the examined complexes.

Pseudohalide complexes [(triphos)Re(CO)$_2$(XCN)] [X = S, (10); Se, (11)]. The redox profile of these complexes is also characterized by the presence of a single oxidation process encompassing the Re^{II}/Re^{I} couple. The Se complex **11** differs from the sulfur analogue **10** in that the redox change **11** → **11**$^+$ is not fully reversible and the i_{pc}/i_{pa} current ratio does not reach a value of unity even at scan rates higher than 5 V s^{-1}. Moreover, the shape of the anodic peak appears slightly rounded, suggesting the possible presence of the two proposed isomers [(triphos)Re(CO)$_2$(η^1-*Se*-SeCN)] (**11**) and [(triphos)Re(CO)$_2$(η^1-*N*-NCSe)] (**11′**). Such a feature is not better resolved in the DPV (differential pulse voltammogram) profile, which also maintains a rounded shape. On the contrary, both **10** and **14** display well-shaped peaks and the redox change is reversible on the CV timescale. Nevertheless, as the

Table 2 Electrochemical properties for selected complexes

[(triphos)Re(CO)$_2$(X)]								
	X	$E^{\circ\prime}$/V	ΔE_p[a]/mV	i_{pc}/i_{pa}[a]	IR $\nu_{initial}$/cm^{-1}	IR ν_{final}/cm^{-1}	Initial colour	Final colour
1	H	0.60[b]	—	—	—	—	Colourless	Violet
2	Cl	0.75	68	0.97	2050, 1960	2140	Pale yellow	Violet
4	Br	0.73	71	0.98	1980, 1915	2030	Pale yellow	Violet
5	I	0.67	77	0.98	—	—	Pale yellow	Violet
8	N_3	0.59	65	0.88	2050, 1970, 1900, 1615	1990, 1930	Pale yellow	Violet
9[c]	μ-N_3	0.79	67	0.47	2080, 1990, 1970, 1925	1990, 1930, 1725	Yellow	Violet
10	SCN	0.76	72	0.92	—	—	Purple	Violet
11	SeCN	0.69	79	0.36	2100, 1980, 1920	—	Pale green	Violet[d]
14/14′[e]	OCN	0.73	70	0.91	2240, 1975, 1910	—	Pale yellow	Violet[e]

[a] At 0.2 V s^{-1}. [b] Registered at 5.0 V s^{-1}. [c] [{(triphos)Re(CO)$_2$}$_2$(μ-N_3)]. [d] Turns golden yellow on standing. [e] Mixture of linkage isomers.

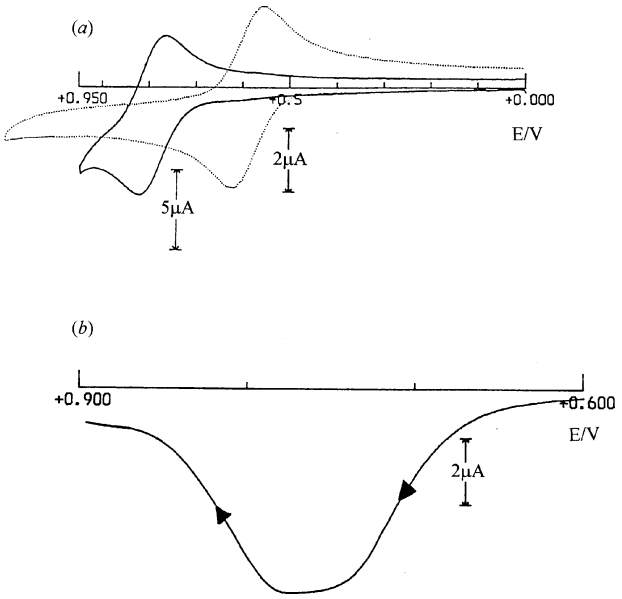


Fig. 3 (*a*) Overlapped cyclic voltammograms of **8** (1.2×10^{-3} M, dotted line) and **9** (7.0×10^{-4} M, full line). Scan rate 0.2 V s^{-1}. (*b*) Differential pulse voltammogram of **9** (7.0×10^{-4} M). Solutions are in CH_2Cl_2–0.2 M NBu_4PF_6. Scan rate 0.004 V s^{-1}.

congener **11** does, they rearrange upon exhaustive oxidation ($E_w = +1$ V) to give rise to a new derivative, which in both cases undergoes a reversible process at $E^{\circ\prime} = +0.70$ V. The progress of the chemical reaction that follows the exhaustive oxidation was monitored by the disappearance of the IR ν(CO) bands.

Azide complexes [(triphos)Re(CO)$_2$(N$_3$)] (8) and [{(triphos)Re(CO)$_2$}$_2$(μ-N$_3$)]OTf (9). The redox behaviour of complexes **8** and **9** is similar to that of the above discussed compounds. In Fig. 3(*a*) the cyclic voltammetric profiles of **8** and **9** are superimposed in order to better appreciate the considerable anodic shift on passing from the monomeric to the dimeric species. This latter complex also exhibits a single oxidation peak, which is assigned to the simultaneous and independent Re^{II}/Re^{I} redox change of both metal sites.

Inspection of the DPV profile [Fig. 3(*b*)] indicates that the two oxidation peaks are not exactly coincident, nevertheless the potential separation is so small that the peaks cannot be clearly distinguished. Therefore, in spite of the highly conjugated pathway offered by the N_3 bridging group, electrochemical data indicate the presence of an extremely weak metal–metal interaction. In both cases the exhaustive oxidation is followed by a rearrangement of the electrogenerated cations: the original colourless solutions turn violet and then golden yellow. No redox active species is obtained upon such a decomposition. IR monitoring of the redox process shows the complete disappearance of both the ν(CO) and the ν(N_3) signals for **8** and **9** together with the growing in of a strong signal at 1725 cm^{-1} for **9**.

A rationale for this behaviour could be found in the cleavage of one (or even two) Re—CO bond(s) after the metal-centred oxidation. Indeed, the $Re^{I} \rightarrow Re^{II}$ oxidation process removes electrons from the t_{2g} metal orbitals involved in the back-donation mechanism with the CO ligands and therefore decreases the Re—CO bond order. A similar behaviour has been previously observed for analogous octahedral Re^{I} species stabilized by π-back-bonding interactions.[37]

Conclusions

A number of new synthetic procedures for preparing the triflate complex [(triphos)Re(CO)$_2$(OTf)] (**3**) are described. The utility of this compound as a synthon of the highly stable rhenium(I) fragment $[(triphos)Re(CO)_2]^+$ is exemplified by the synthesis of a variety of mononuclear and binuclear halide and pseudohalide complexes. Among the new complexes are the first dirhenium(I) species featuring bridging azido, thio- and selenocyanate ligands. Regioselective alkylation of the chalcogenocyanate derivatives affords unprecedented examples of methylsulfide- and methylselenide-cyanide rhenium complexes. Studies are in progress to define the synthetic scope of the electrophilic alkylation of **10** and **11** better and to verify if the unusual S(Me)(CN) and Se(Me)(CN) ligands may be removed from the co-ordination sphere of the metal and used in organic and organometallic synthesis.

Experimental

Materials and methods

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$ before use; *n*-hexane was stored over molecular sieves and purged with nitrogen prior to use. All other reagents and chemicals were commercial products and were used as received without further purification; [(triphos)Re(CO)$_2$(Cl)] (**2**) was prepared as previously reported.[1a]

IR spectra were obtained in KBr using a Nicolet 510 P FT-IR (4000–200 cm^{-1}) spectrophotometer. Deuteriated solvents for NMR measurements (Aldrich and Merck) were dried over molecular sieves (4 Å). Proton NMR spectra were recorded on Bruker AC200 or Varian VXR300 instruments operating at 200.13 and 299.94 MHz, respectively. Peak positions are relative to tetramethylsilane (TMS) as an external reference or were calibrated with respect to the residual protiated solvent. $^{31}P\{^1H\}$ NMR spectra were recorded at 81.01 and 121.42 MHz, on the same instruments, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were recorded on the Bruker AC200P instrument at 50.32 MHz and 188.3 MHz, respectively. The chemical shifts are relative to TMS for $^{13}C\{^1H\}$ and to external $CFCl_3$ for $^{19}F\{^1H\}$ NMR.

The spin-lattice relaxation time (T_1) on the cyanide binuclear complex **7** was measured in dichloromethane at 300 MHz by the inversion-recovery method using the standard 180°–τ–90° pulse sequence. The calculations of the relaxation times were made using the fitting routine of the Varian VXR300 spectrometer. The 90 degree pulse on the sample of **7** was carefully measured before running the T_1 measurements. The computer simulation of the $^{13}C\{^1H\}$ NMR spectra was carried out with a locally developed package containing the programs LAOCN3[38] and DAVINS.[39] The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using the experimental digitized spectrum. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor being less than 1% in all cases.

Molar conductivities were measured with an AMEL model 134 conductance cell connected with a model 101 conductivity meter. The conductivity data were obtained at sample concentrations of 10^{-3} M in nitroethane solutions at room temperature (22 °C). Elemental analyses (C, H, N, S) were performed using a Carlo Erba model 1106 elemental analyser. Mass spectra were recorded on a Hewlett Packard MS Engine HP 5989A. For the FAB measurements, xenon was used as the primary beam gas. The ion gun was operated at 8 kV and 10 μA (probe temperature 50 °C); nitrobenzyl alcohol was used as the matrix. Materials and apparatus for electrochemistry have been described elsewhere.[40] Voltammetric (cyclic and differential pulse) and coulometric techniques coupled

with IR spectroscopy have been used to characterize both the redox behaviour and the stability of the electrogenerated species. All of the measurements were done at a platinum electrode in dichloromethane using NBu_4PF_6 (0.2 M) as the supporting electrolyte. The potentials are referred to SCE.

Synthesis of [(triphos)Re(CO)$_2$(OTf)] (3)

Method 1. A Schlenk tube was charged with **2** (2.0 g, 2.21 mmol) and dichloromethane (15 mL). The resulting solution was cooled to −10 °C with an ice–salt bath and stirred under N_2 before adding an excess of MeOTf (377 μL, 3.32 mmol) *via* a microsyringe. The starting material dissolved in a few minutes to give a clear yellow solution. The cooling bath was removed and the solution was stirred at room temperature for 15 min. The reaction mixture was concentrated to *ca.* 6 mL under vacuum. Addition of diethyl ether (5 mL) precipitated a pale yellow powder, which was filtered off, washed with diethyl ether (2 × 3 mL) and dried under vacuum. Yield 95%.

Method 2. To a solution of **2** (200.0 mg, 0.22 mmol) in dichloromethane (10 mL) was added 1.1 equiv. of AgOTf (70.0 mg, 0.27 mmol). The mixture was stirred for 1 h and then silver chloride was removed by filtering the grey suspension through Celite, which was then washed with dichloromethane (2 × 3 mL). The combined filtrate and washings were evaporated to dryness under vacuum. The solid residue was extracted with 5 mL of dichloromethane. Concentration of the resulting yellow solution and addition of *n*-hexane (3 mL) gave a pale yellow product, which was filtered off, washed with diethyl ether (2 × 3 mL) and dried under vacuum. Yield 85%.

Method 3. A slight excess of HOTf (6 μL, *ca.* 6.6×10^{-2} mmol) was added *via* syringe to a solution of **2** (50 mg, 5.5×10^{-2} mmol) in dichloromethane-d_2 (1.0 mL) in a 5 mm NMR tube. $^{31}P\{^1H\}$ and ^1H NMR spectroscopy showed the quantitative formation of **3**.

Method 4. HOTf (56 μL, 0.63 mmol) was added under nitrogen to a stirred suspension of [(triphos)Re(CO)$_2$(H)] (**1**) (500.0 mg, 0.57 mmol) in dichloromethane (15 mL) cooled to −10 °C. Stirring was continued for 5 min during which time all the monohydride dissolved to produce a pale yellow solution, which was slowly brought to room temperature. After 1 h stirring, addition of *n*-hexane (10 mL) yielded **3** as a pale yellow product. Monitoring the reaction by ^1H and ^{31}P NMR spectroscopy showed that the formation of **3** is at the beginning accompanied by the agostic complex [(triphos)Re(CO)$_2$]OTf.[1a] This completely transformed into **3** over 1 h. Anal. found: C, 52.00; H, 3.90; S, 3.12. Calcd for $C_{44}H_{39}F_3O_5P_3SRe$: C, 52.02; H, 3.87; S, 3.16%. IR: ν(CO) 1967, 1902; ν(η^1-OSO_2CF_3) 1320 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A 6.20, δ_M − 10.11; J_{AM} 14.7 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.54 (br s, CH_3, 3H), 2.55 (m, CH_2, 6H). ^{19}F NMR (295 K, CD_2Cl_2): −77.55 (s, η^1-OSO_2CF_3). $^{13}C\{^1H\}$ NMR (295 K, CD_2Cl_2): δ 197.5 (AXX′Y spin system, J_{AX} 52.8, $J_{AX'}$ − 8.2, J_{AY} 6.6, $J_{XX'}$ 26.5 Hz, *C*O); 39.9 (q, J_{CP} 9.9 Hz, *C*H$_3$C), 39.4 (q, J_{CP} 3.3 Hz, CH$_3$*C*), 37.9 (dt, J_{CPax} 28.0, J_{CPeq} 4.0 Hz, *C*H$_2$P$_{ax}$), 33.7 [td, N = ($J_{CPeq'}$ + $J_{CPax''}$) 15.7, J_{CPax} 5.1 Hz, *C*H$_2$P$_{eq}$].

Synthesis of the halide complexes

[(triphos)Re(CO)$_2$(Br)] (4). An excess of KBr (117.2 mg, 0.98 mmol) was added at room temperature under vigorous stirring to a suspension of **3** (200.0 mg, 0.19 mmol) in 20 mL of THF. The mixture was stirred for 18 h, the solvent was removed under reduced pressure and the resulting yellow solid was extracted with two 5 mL portions of dichloromethane. The extracts were concentrated to half their volume and 5 mL of *n*-hexane was added to give white microcrystals, which were collected by filtration, washed with diethyl ether and dried under reduced pressure. Yield 73%. Anal. found: C, 53.98; H, 4.08. Calcd for $C_{43}H_{39}BrO_2P_3Re$: C, 54.55; H, 4.15%. IR: ν(CO) 1950, 1889 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A 2.15, δ_M − 20.14, J_{AM} 14.6 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.42 (q, J_{HP} 2.4 Hz, CH_3, 3H), 2.42 (m, CH_2, 6H).

[(triphos)Re(CO)$_2$(I)] (5). The iodide derivative was prepared as described above by replacing KBr with KI (157.7 mg, 0.95 mmol). Complex **5** was isolated as a pale yellow product in *ca.* 90% yield. Anal. found. C, 51.86; H, 4.00. Calcd for $C_{43}H_{39}IO_2P_3Re$: C, 51.97; H, 3.96%. IR: ν(CO) 1950, 1892 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A − 0.12, δ_M − 24.7, J_{AM} 15.2 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.40 (q, J_{HP} 2.5 Hz, CH_3, 3H), 2.22 (m, CH_2, 6H).

Attempted synthesis of [(triphos)Re(CO)$_2$(F)]. No reaction was observed when **3** and different sources of fluoride ion [NaF, KF or (PPN)F] were allowed to react under the reaction conditions reported above.

Synthesis of the pseudohalide complexes

[(triphos)Re(CO)$_2$(CN)] (6). To a stirred suspension of **3** (200.0 mg, 0.19 mmol) in 20 mL of THF at room temperature, a five-fold excess of tetrabutylammonium cyanide (264.4 mg, 0.95 mmol) was added. The starting material dissolved within a few minutes to give a clear yellow solution. After 1 h stirring, the volume was reduced to *ca.* 5 mL. Slow addition of *n*-hexane (5 mL) gives a yellow precipitate, which was collected by filtration, washed with diethyl ether and dried under reduced pressure. Yield 75%. Anal. found: C, 59.10; H, 4.38; N, 1.51. Calcd for $C_{44}H_{39}NO_2P_3Re$: C, 59.18; H, 4.40; N, 1.56%. IR: ν(CN) 2106, ν(CO) 1946, 1890 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A − 5.90, δ_M − 17.88, J_{AM} 18.4 Hz. ^1H NMR (295 K, $CDCl_3$): 1.46 (br s, CH_3, 3H), 2.40 (m, CH_2, 6H). $^{13}C\{^1H\}$ NMR (295 K, $CDCl_3$): δ 195.0 (m, *C*O), 131.4 (d, $^2J_{CP\ trans}$ 10.9 Hz, *C*N), 40.2 (q, J_{CP} 9.9 Hz, *C*H$_3$C), 39.2 (q, J_{CP} 3.3 Hz, CH$_3$*C*), 35.2 (m, *C*H$_2$P$_{ax}$), 33.3 (m, *C*H$_2$P$_{eq}$).

[{(triphos)Re(CO)$_2$}$_2$(μ-CN)]OTf (7). *Method 1.* The binuclear complex **7** was prepared, in almost quantitative yield, from the reaction of the monomeric complex **6** (100.0 mg, 0.11 mmol) with 1 equiv. of **3** (113.7 mg) in dichloromethane (5 mL) at room temperature. The resulting solution was stirred for 15 min during which time the originally pale yellow solution turned colourless. Addition of 5 mL of *n*-hexane caused the precipitation of **7** as white microcrystals. These were collected by filtration and washed with *n*-hexane and diethyl ether before being dried under nitrogen. Yield 90%.

Method 2. Compound **7** was obtained also by treating a suspension of **3** (200.0 mg, 0.19 mmol) in THF (20 mL) with 0.5 equiv of [Bu_4N]CN (25.5 mg). Yield *ca.* 80%. Anal. found: C, 55.70; H, 4.15; N, 0.74; S, 1.70. Calcd for $C_{88}H_{78}F_3NO_7P_6Re_2S$: C, 55.37; H, 4.12; N, 0.73; S, 1.68%. IR: ν(CN) 2097; ν(CO) 1967, 1908; ν(OTf^-) 1275 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): $AA'M_2M'_2$ spin system, δ_A 0.21, $\delta_{A'}$ − 7.41, δ_M − 17.12, $\delta_{M'}$ − 17.66, J_{AM} 16.3, $J_{A'M'}$ 19.5, $J_{AA'} = J_{MM'} = J_{A'M} = J_{AM'}$ 0 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.49 (q, J_{HP} 2.4 Hz, CH_3, 3H), 1.56 (s, CH_3, 3H), 2.6–2.2 (m, CH_2, 12H). $\Lambda_{M(nitroethane)}$ = 43.3 Ω^{-1} cm^2 mol^{-1}. FAB$^+$-MS: *m*/*z* 1760 (M^+), 893 [(triphos)Re(CO)$_2$CN]$^+$, 867 [(triphos)Re(CO)$_2$]$^+$, 839 [(triphos)Re(CO)]$^+$.

[{(triphos)Re(CO)$_2$}$_2$(μ-CN)]BPh$_4$ (7-BPh$_4$). A solution of $NaBPh_4$ (26.9 mg, 7.8×10^{-2} mmol) in methanol (5 mL) was added to **7** (100.0 mg, 5.2×10^{-2} mmol) dissolved in dichloro-

methane (5 mL). After 30 min stirring, the white solid formed was collected on a filter, washed with methanol and diethyl ether and dried under vacuum. Anal. found: C, 64.20; H, 4.80; N, 0.71. Calcd for $C_{111}H_{98}BNO_4P_6Re_2$: C, 64.13; H, 4.75; N, 0.67%. The IR spectrum showed the characteristic band at 610 cm^{-1} due to $\nu(BPh_4)$.

[(triphos)Re(CO)$_2$(N$_3$)] (8). An excess of $(PPN)N_3$ (341.2 mg, 0.57 mmol) was added to a stirred dichloromethane (5 mL) solution of **3** (200 mg, 0.19 mmol). An immediate colour change from yellow to deep red was observed while stirring was continued additionally for 15 min. Addition of diethyl ether (5 mL) gave **8** as yellow microcrystals. The compound was collected on a sintered glass frit, washed with diethyl ether and dried under vacuum. Yield 75%. Anal. found: C, 56.80; H, 4.30; N, 4.59. Calcd for $C_{43}H_{39}N_3O_2P_3Re$: C, 56.82; H, 4.32; N, 4.62%. IR: $\nu_{as}(N_3)$ 2044; ν(CO) 1936, 1879; $\nu_{sym}(N_3)$ 1334 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A 1.07, δ_M − 15.07, J_{AM} 14.9 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.48 (br s, CH_3, 3H), 2.48 (m, CH_2, 6H).

Monitoring the reaction of 3 with PPN(N$_3$) by $^{31}P\{^1H\}$ NMR spectroscopy. Monitoring the reaction between **3** (30 mg, 2.9×10^{-2} mmol) and a stoichiometric amount of $(PPN)N_3$ (17.6 mg, 2.9×10^{-2} mmol) in a 5 mm NMR tube (1.0 mL of dichloromethane-d_2) by ^{31}P NMR spectroscopy showed that **8** is formed together with the binuclear derivative **9** (*ca.* 10 : 1 ratio). The composition of the mixture does not change over a week and is temperature invariant.

[{(triphos)Re(CO)$_2$}$_2$(μ-N$_3$)]OTf (9). The dinuclear complex **9** was obtained as white microcrystals by combining **3** (200.0 mg, 0.19 mmol) with 0.5 equiv of $(PPN)N_3$ (55.1 mg) in dichloromethane (10 mL) at room temperature. The colour of the solution immediately became deep red, but in a few minutes turned to deep yellow. After 30 min stirring the solution was evaporated under nitrogen to *ca.* 5 mL. Addition of diethyl ether (5 mL) gave **9**. Yield 77%. Anal. found: C, 54.30; H, 4.00; N, 2.17; S, 1.64. Calcd for $C_{87}H_{78}F_3N_3O_7P_6Re_2S$: C, 54.29; H, 4.08; N, 2.18; S, 1.67%. IR: $\nu(N_3)$ 2122; ν(CO) 1952, 1894; ν(OTf) 1272 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): $(AM_2)_2$ spin systems, δ_A 0.75, δ_M − 11.96, J_{AM} 16.3 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.51 (br s, CH_3, 6H), 2.50 (m, CH_2, 12H). $\Lambda_{M(nitroethane)} = 57.4\ \Omega^{-1}\ cm^2\ mol^{-1}$. FAB^+-MS: *m/z* 1775 (M^+), 909 $[(triphos)Re(CO)_2N_3]^+$, 867 $[(triphos)Re(CO)_2]^+$, 839 $[(triphos)Re(CO)]^+$.

[{(triphos)Re(CO)$_2$}$_2$(μ-N$_3$)]BPh$_4$ (9-BPh$_4$). Metathetical reaction of **9** (100.0 mg, 5.2×10^{-2} mmol) with an excess of $NaBPh_4$ (26.7 mg, *ca.* 7.8×10^{-2} mmol) in dichloromethane–methanol (1 : 1 v/v, 8 mL) gave $[\{(triphos)Re(CO)_2\}_2\mu\text{-}N_3)]BPh_4$ as white microcrystals. Yield 90%.

Thermal behaviour of [(triphos)Re(CO)$_2$(N$_3$)] (8) and [{(triphos)Re(CO)$_2$}$_2$(μ-N$_3$)]OTf (9). On refluxing either **8** or **9** in THF, no reaction took place over a period of 12 h ($^{31}P\{^1H\}$ NMR monitoring).

[(triphos)Re(CO)$_2$(η^1-*S*-SCN)] (10). Solid NH_4SCN (72 mg, 0.95 mmol) was added to a stirred suspension of **3** (200 mg, 0.19 mmol) in 20 mL of THF. The resulting mixture, which immediately turned deep red, was stirred for 4 h and concentrated to dryness. The crude material was extracted twice with dichloromethane (2 mL) and filtered to remove excess ammonium thiocyanate. Concentration of the combined extracts and addition of diethyl ether (5 mL) gave a purple product, which was filtered off and dried under oil pump vacuum. The crude product was recrystallized from dichloromethane–diethyl ether to yield purple microcrystals of **10**. Yield 85%. Anal. found: C, 57.15; H, 4.23; N, 1.50; S, 3.44. Calcd for $C_{44}H_{39}NO_2P_3ReS$: C, 57.13; H, 4.25; N, 1.51; S, 3.47%. IR: ν(SCN) 2106; ν(CO) 1956, 1900 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A − 2.42, δ_M − 15.95, J_{AM} 17.0 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.53 (q, J_{HP} 2.4 Hz, CH_3, 3H), 2.53 (m, CH_2, 6H). $^{13}C\{^1H\}$ NMR (295 K, CD_2Cl_2): δ 197.4 (m, *C*O), 124.5 (br s, S*C*N), 41.4 (q, J_{CP} 10.1 Hz, *C*H$_3$C), 41.0 (q, J_{CP} 3.8 Hz, CH$_3$*C*), 37.0 (dt, J_{CPax} 26.9, J_{CPeq} 3.0 Hz, *C*H$_2$P$_{ax}$), 35.7 [td, $N = (J_{CPeq'} + J_{CPax''})$ 14.3; J_{CPax} 5.5 Hz, *C*H$_2$P$_{eq}$]. FAB^+-MS: *m/z* 925 (M^+), 867 $[(triphos)Re(CO)_2]^+$, 839 $[(triphos)Re(CO)]^+$.

Monitoring the reaction of NH$_4$SCN with 3 by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR monitoring of the reaction between **3** (30.0 mg, 2.9×10^{-2} mmol) and one equivalent of NH_4SCN (2.2 mg, 2.9×10^{-2} mmol) in a 5 mm NMR tube (1.0 mL of THF-d_8) showed that the formation of **10** (*ca.* 70%) is accompanied by two new sets of resonances ascribable to the *N*-bonded thiocyanate isomer, **10′** (*ca.* 20%), and to the dinuclear complex **12** (*ca.* 10%, see below for the NMR characterization), respectively. On heating the NMR tube at 60 °C, the transformation of **10′** into **10** was completed in 3 days. $^{31}P\{^1H\}$ NMR (295 K, THF-d_8) of **10′**: AM_2 spin system, δ_A 0.07, δ_M − 15.58; J_{AM} 17.1 Hz. On concentrating the NMR tube solution to dryness, a purple powder was obtained, which in the IR spectrum exhibited a sharp band at 2077 cm^{-1} assignable to ν(NCS) in the *N*-bonded isomer **10′**.

[{(triphos)Re(CO)$_2$}$_2$(μ-η^1-*S*,η^1-*N*-SCN)]OTf (12). *Method 1.* To a stirred solution of **3** (200.0 mg, 0.19 mmol) in THF (20 mL), 0.5 equivalent of solid NH_4SCN (7.2 mg, 0.095 mmol) was added. The initial yellow colour immediately disappeared to produce a deep purple solution, which was stirred for 1 h. Concentration of the solution under nitrogen and addition of diethyl ether (5 mL) gave purple microcrystals of **12**, which were filtered off and washed with diethyl ether before being dried under nitrogen. Yield 85%.

Method 2. One equivalent of **3** (109.8 mg, 0.10 mmol) was added under vigorous stirring to a dichloromethane solution (5 mL) of **10** (100.0 mg, 0.10 mmol). After 1 h stirring, concentration under nitrogen and addition of *n*-hexane (10 mL) gave purple microcrystals of **12**. Yield 75%. Anal. found: C, 54.55; H, 4.06; N, 0.75; S, 3.28. Calcd for $C_{88}H_{78}F_3NO_7P_6Re_2S_2$: C, 54.46; H, 4.05; N, 0.72; S, 3.30%. IR: ν(SCN) 2140; ν(CO) 1958, 1900; ν(OTf) 1273 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): $AA'M_2M'_2$ spin systems, δ_A − 2.13, $\delta_{A'}$ − 2.52, δ_M − 12.90, $\delta_{M'}$ − 14.70; $J_{AM} = J_{A'M'}$ 18.3, $J_{AA'} = J_{MM'} = J_{A'M} = J_{AM'}$ 0 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.72 (br s, CH_3, 6H), 2.4–2.6 (m, CH_2, 12H). $\Lambda_{M(nitroethane)} = 48.5\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[{(triphos)Re(CO)$_2$}$_2$ (μ-η^1-*S*,η^1-*N*-SCN)]BPh$_4$ (12-BPh$_4$). Metathetical reaction of **12** (100.0 mg, 5.1×10^{-2} mmol) in dichloromethane (5 mL) with excess $NaBPh_4$ (26.4 mg, 7.7×10^{-2} mmol) in ethanol (2 mL) gave **12**-BPh_4 in almost quantitative yield. Anal. found: C, 63.20; H, 4.70; N, 0.64; S, 1.49. Calcd for $C_{111}H_{98}BNO_4P_6Re_2S$: C, 63.0.8; H, 4.68; N, 0.66; S, 1.51%. IR: ν(SCN) 2140; ν(CO) 1958, 1900; $\nu(BPh_4)$ 610 cm^{-1}.

[(triphos)Re(CO)$_2$(η^1-*Se*-SeCN)] (11). On replacing NH_4SCN with KSeCN (85 mg, 0.60 mmol) in the preparation of **10**, deep green microcrystals of **11** were obtained after usual work-up. Recrystallization from dichloromethane–diethyl ether gave **11** in analytically pure form. Yield 75%. Anal. found: C, 54.25; H, 3.99; N, 1.39. Calcd for $C_{44}H_{39}P_3ReO_2SeN$: C, 54.38; H, 4.04; N, 1.44%. IR: ν(SeCN) 2116; ν(CO) 1958, 1898 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A − 3.41, δ_M − 16.18, J_{AM} 17.4 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.50 (q, J_{HP} 2.3 Hz, CH_3, 3H), 2.47 (m, CH_2, 6H). $^{13}C\{^1H\}$ NMR (295 K, CD_2Cl_2): δ 197.9

(AXX′Y spin system, J_{AX} 55.6, $J_{AX'}$ − 8.8, J_{AY} 7.1, $J_{XX'}$ 28.5 Hz, *C*O), 108.9 (q, J_{CP} 3.4 Hz, Se*C*N), 40.1 (q, J_{CP} 10.0 Hz, *C*H$_3$C), 39.8 (q, J_{CP} 3.2 Hz, CH$_3$*C*), 35.4 (dt, J_{CPax} 26.3, J_{CPeq} 3.1 Hz, *C*H$_2$P$_{ax}$), 34.3 [td, $N = (J_{CPeq'} + J_{CPax''})$ 15.3; J_{CPax} 4.9 Hz, *C*H$_2$P$_{eq}$].

Monitoring the reaction of KSeCN with 3 by $^{31}P\{^1H\}$ NMR spectroscopy. Monitoring the reaction between **3** (40 mg, 3.9×10^{-2} mmol) and one equivalent of KSeCN (5.7 g, 3.9×10^{-2} mmol) in a 5 mm NMR tube (1.0 mL of THF-d_8) as described above for the thiocyanate analogue showed that the formation of **11** (45%) is accompanied by that of the *N*-bonded selenocyanate isomer, **11′** (10%), and the dinuclear compex **13** (45%, see below for the NMR properties). On heating the NMR tube at 60 °C, the transformation of **11′** into **11** was completed in one day. $^{31}P\{^1H\}$ NMR (295 K, THF-d_8) of **11′**: AM_2 spin system, δ_A − 0.23, δ_M − 15.01; J_{AM} 16.0 Hz. On concentrating the NMR tube solution to dryness, a pale green powder was obtained, which in the IR spectrum exhibits a sharp band at 2066 cm^{-1} characteristic of ν(NCSe) in the *N*-bonded isomer **10′**.

[{(triphos)Re(CO)$_2$}$_2$(μ-η^1-*Se*,η^1-*N*-SeCN)]OTf (13). Bluish violet microcrystals of **13** were isolated following a procedure identical to that described for **12**, using KSeCN (14.2 mg) instead of NH_4SCN. The colour of the solution immediately became deep green, but after a few minutes, turned blue. Yield 75%. Anal. found: C, 53.00; H, 3.91; N, 0.68; S, 1.58. Calcd for $C_{88}H_{78}F_3NO_7P_6Re_2SSe$: C, 53.09; H, 3.95; N, 0.70; S, 1.61%. IR: ν(SeCN) 2142; ν(CO) 1960, 1900; ν(OTf) 1271 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): $AA'M_2M'_2$ spin systems, δ_A −2.18, $\delta_{A'}$ −3.47, δ_M −12.90, $\delta_{M'}$ −15.97, $J_{AM} = J_{A'M'}$ 18.1, $J_{AA'} = J_{MM'} = J_{A'M} = J_{AM'}$ 0 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.68 (br s, CH_3, 6H), 2.47 (m, CH_2, 12H). $\Lambda_{M(nitroethane)} = 67.6\ \Omega^{-1}\ cm^2\ mol^{-1}$.

[{(triphos)Re(CO)$_2$}$_2$(μ-η^1-*Se*,η^1-*N*-Se(CN)]BPh$_4$ (13-BPh$_4$). Metathetical reaction of **13** (100.0 mg, 5.0×10^{-2} mmol) in dichloromethane (5 mL) with excess of $NaBPh_4$ (25.8 mg, 7.5×10^{-2} mmol) in ethanol (2 mL) gave the tetraphenylborate salt **13**-BPh$_4$ in almost quantitative yield. Anal. found: C, 61.61; H, 4.54; N, 0.62. Calcd for $C_{111}H_{98}BNO_4P_6Re_2Se$: C, 61.68; H, 4.57; N, 0.65%. IR: ν(SeCN) 2142; ν(CO) 1960, 1900; ν(BPh$_4$) 610 cm^{-1}.

Preparation of the isomeric mixture [(triphos)Re(CO)$_2$(η^1-*N*-NCO)] (14) and [(triphos)Re(CO)$_2$(η^1-*O*-NCO)] (14′). A suspension of **3** (200.0 mg, 0.19 mmol) in 20 mL of THF was treated with a five-fold excess of NaOCN (64.0 g, 1.0 mmol) and stirred at room temperature for 12 h without any change of colour. Addition of *n*-hexane (20 mL) and concentration under nitrogen yielded a pale yellow precipitate, which was washed with diethyl ether and dried under vacuum. Yield 70%. The $^{31}P\{^1H\}$ NMR analysis of the crude product indicates the formation of a mixture of the two complexes **14** (70%) and **14′** (30%). Anal. found: C, 58.20; H, 4.35; N, 1.52. Calcd for $C_{44}H_{39}P_3ReO_3N$: C. 58.14; H, 4.32; N, 1.54%. IR: ν_{as}(NCO) 2234; ν(CO) 1950, 1886 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): **14**, AM_2 spin system, δ_A 1.79, δ_M −16.42, J_{AM} 15.3 Hz; **14′**, AM_2 spin system, δ_A 3.75, δ_M −18.94, J_{AM} 13.7 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.48 (br s, CH_3, 3H of **14** and **14′**), 2.5–2.4 (m, CH_2, 6H of **14** and **14′**).

Electrophilic alkylation reations

[(triphos)Re(CO)$_2$(CNCH$_3$)]OTf (15). A Schlenk tube was charged with **6** (100.0 mg, 0.11 mmol) dissolved in dichloromethane (10 mL) and MeOTf (14 μL, 0.12 mmol) was added under vigorous stirring with a syringe. Evaporation of the solution to dryness under vacuum gave **15**, as a yellow powder. The crude product was recrystallized by dichloromethane and ethanol (1 : 1 v/v). Yield 90%. Anal. found: C, 52.20; H, 4.03; N, 1.28; S, 3.01. Calcd for $C_{46}H_{42}F_3NO_5P_3ReS$: C, 52.27; H, 4.00; N, 1.33; S, 3.03%. IR: ν(CN) 2184; ν(CO) 1971, 1915; ν(OTf) 1269 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): AM_2 spin system, δ_A −12.04, δ_M −14.15, J_{AM} 21.5 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.65 (br q, J_{HP} 2.9 Hz, CH_3, 3H), 2.57 (m, CH_2, 6H), 3.06 (s, $CNCH_3$, 3H).

[(triphos)Re(CO)$_2${η^1-*S*-S(CH$_3$)(CN)}]OTf (16). On replacing **6** with **10** in the above procedure, **16** was obtained as pale yellow microcrystals. Yield *ca.* 90%. Anal. found: C, 50.65; H, 3.90; N, 1.28; S, 5.90. Calcd for $C_{46}H_{42}F_3NO_5P_3ReS_2$: C, 50.73; H, 3.89; N, 1.29; S, 5.89%. IR: ν(SCN) 2139; ν(CO) 1956, 1900; ν(OTf) 1267 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): δ_A −5.19, δ_M −10.52, J_{AM} 19.2 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.65 (br q, J_{HP} 2.9 Hz, CH_3, 3H), 2.8–2.4 (m, CH_2, 6H), 2.30 (s, SCH_3, 3H).

[(triphos)Re(CO)$_2${η^1-*Se*-Se(CH$_3$)CN)}]OTf (17). On replacing **10** with **11** in the above procedure, **17** was obtained as pale yellow microcrystals. Yield *ca.* 90%. Anal. found: C, 48.60; H, 3.75; N, 1.26; S, 2.80. Calcd for $C_{46}H_{42}F_3NO_5P_3ReSSe$: C, 48.64; H, 3.73; N, 1.23; S, 2.82%. IR: ν(SeCN) 2183; ν(CO) 1956, 1898; ν(OTf) 1271 cm^{-1}. $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl): δ_A −4.60, δ_M −9.93, J_{AM} 19.6 Hz. ^1H NMR (295 K, CD_2Cl_2): 1.65 (br q, J_{HP} 2.9 Hz, CH_3, 3H), 2.85–2.45 (m, CH_2P_{eq}, 4H), 2.57 (d, J_{HP} 10.6, CH_2P_{ax}, 2H), 2.28 (s, $SeCH_3$, 3H; this signal exhibits ^{77}Se satellites with $^2J_{HSe}$ = 13.1 Hz).

***In situ* NMR studies**

Reaction of 2 with Me$_3$OBF$_4$ (Scheme 2). A 5 mm NMR tube was charged with 30.0 mg (3.3×10^{-2} mmol) of **2** in THF-d_8 (0.8 mL). The tube was cooled down to −78 °C with a liquid nitrogen–isopropanol bath and Me_3OBF_4 (10.0 mg, 6.6×10^{-2} mmol) in 0.2 mL of THF-d_8 was added with a syringe. The tube was inserted into the spectrometer cooled to −60 °C and a $^{31}P\{^1H\}$ NMR spectrum was immediately recorded. It showed the formation of the agostic cation complex $[(triphos)Re(CO)_2]^+$ (80%)[1a] together with some $[(triphos)Re(CO)_2(\eta^1\text{-}O\text{-THF-}d_8)]^+$ (20%); $^{31}P\{^1H\}$ NMR (295 K, CD_2Cl_2): δ_A 3.76, δ_M −18.88, J_{AM} 13.73 Hz.[11]

Reaction of 2 with MeOTf (Scheme 2). A 5 mm NMR tube was charged with the chloride complex **2** (30.0 mg, 3.3×10^{-2} mmol) in $CDCl_3$ (0.8 mL) and capped with a septum. The tube was immersed in a liquid nitrogen bath and MeOTf (4 μL, *ca.* 3.3×10^{-2} mmol) was added with a syringe before inserting the tube into the probe of the NMR spectrometer precooled to −60 °C. The $^{31}P\{^1H\}$ spectrum showed the formation of [(triphos)Re(CO)$_2$(OTf)] (**3**) as the only product, while the ^1H NMR spectrum featured a singlet at *ca.* 3.0 ppm attributed to free CH_3Cl. On repeating the same *in situ* NMR experiment with the bromide and the iodide derivatives **4** and **5**, stoichiometric formation of CH_3Br (δ 2.68) and CH_3I (δ 2.15) was observed, respectively.

Reaction of 11 with MeOTf. A 5 mm NMR tube was charged with the selenocyanate complex **11** (25 mg, 2.6×10^{-2} mmol) in dichloromethane-d_2 (10 mL) and capped with a septum. The tube was cooled down to −78 °C and MeOTf (4.4 μL, 3.8×10^{-2} mmol) was added with a syringe. The tube was shaken and inserted into the NMR probehead pre-cooled to −30 °C and a $^{31}P\{^1H\}$ NMR spectrum was immediately recorded. It showed the formation of **17** (70%) and of the *N*-alkylated isomer [(triphos)Re(CO)$_2${η^1-*Se*-Se(Me)(CN)}]OTf (**18**) (30%). On standing at low temperature, **18** transforms into **17** within one night. The transformation is completed in 1 h at room temperature. $^{31}P\{^1H\}$ NMR (243 K,

CD_2Cl_2) of **18**: AM_2 spin system, δ_A −3.53, δ_M −13.10, J_{AM} 18.2 Hz.

Reaction of [(triphos)Re(CO)$_2$(N$_3$)] and [(triphos)Re(CO)$_2$(NCO)] with MeOTf

Repeating the electrophilic methylation on either the azide (**8**) or the cyanate complex (**14**) gave the triflate complex **3** in quantitative yield. Monitoring of both the reactions by NMR spectroscopy did not give further information about the reaction mechanisms and did not disclose any intermediate species.

Acknowledgements

We are grateful to the EC (ERBIC15CT960746) for financial support. Thanks are expressed to Mr M. Fratta (University of Ferrara) for technical assistance and elemental analyses, to Mr E. Angeli (University of Ferrara) for the FAB measurements, and to Professor A. Romerosa (University of Almeria, Spain) for helpful discussions.

Notes and references

1 (*a*) C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa, R. Rossi and A. Vacca, *Organometallics*, 1995, **14**, 3203; (*b*) C. Bianchini, A. Marchi, L. Marvelli, M. Peruzzini, A. Romerosa and R. Rossi, *Organometallics*, 1996, **15**, 3804; (*c*) C. Bianchini, A. Marchi, N. Mantovani, L. Marvelli, D. Masi, M. Peruzzini and R. Rossi, *Eur. J. Inorg. Chem.*, 1998, 211.
2 G. A. Lawrance, *Chem. Rev.*, 1986, **86**, 17.
3 The use of inorganic triflates as active Lewis acids and catalysts is witnessed by the large number of these salts listed in the catalogues of some of the most important chemical suppliers. See for example: *1998-1999 Inorganics & Organometallics Catalog/Handbook*, Aldrich Co, 1998.
4 J. H. Merrifield, J. M. Fernandez, W. E. Buhro and J. A. Gladysz, *Inorg. Chem.*, 1984, **23**, 4022.
5 M. Peruzzini and L. Marvelli, unpublished results.
6 D. G. Gusev, A. B. Vymenits and V. I. Bakhmutov, *Mendeleev Commun.*, 1991, 24.
7 E. S. Shubina, N. V. Belkova, E. V. Bakhmutova, E. V. Vorontsov, V. I. Bakhmutov, A. V. Ionidis, C. Bianchini, L. Marvelli, M. Peruzzini and L. M. Epstein, *Inorg. Chim. Acta*, 1998, **280**, 302.
8 (*a*) A. C. Filippou and E. O. Fischer, *J. Organomet. Chem.*, 1988, **352**, 149; (*b*) K. H. Griessmann, A. Stasunik, W. Angerer and W. Malisch, *J. Organomet. Chem.*, 1986, **303**, C29.
9 R. J. Kulawiec and R. H. Crabtree, *Coord. Chem. Rev.*, 1990, **99**, 89.
10 (*a*) C. H. Winter, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1987, **109**, 7560; (*b*) C. H. Winter and J. A. Gladysz *J. Organomet. Chem.*, 1988, **354**, C33; (*c*) J. Fernandez and J. A. Gladysz, *Organometallics*, 1989, **8**, 207.
11 M. Peruzzini and L. Marvelli, unpublished results.
12 N. M. Doherty and N. W. Hoffman, *Chem. Rev.*, 1991, **91**, 553.
13 (*a*) N. W. Hoffman, N. Prokopuk, M. J. Robbins, C. M. Jones and N. M. Doherty, *Inorg. Chem.*, 1991, **30**, 4177; (*b*) P. W. Blosser, J. C. Gallucci and A. Wojcicki, *Inorg. Chem.*, 1992, **31**, 2376.
14 See ref. 1. Other octahedral triphos complexes of rhenium include: (*a*) C. Bianchini, M. Peruzzini, F. Zanobini, L. Magon, L. Marvelli and R. Rossi, *J. Organomet. Chem.*, 1993, **451**, 97; (*b*) M. T. Costello, P. E. Fanwick, M. A. Green and R. A. Walton, *Inorg. Chem.*, 1992, **31**, 2359.
15 See also: (*a*) C. Bianchini, K. G. Caulton, T. J. Johnson, A. Meli, M. Peruzzini and F. Vizza, *Organometallics*, 1995, **14**, 933; (*b*) C. Bianchini, M. Peruzzini, A. Vacca and F. Zanobini, *Organometallics*, 1991, **10**, 3697.
16 C. Bianchini, A. Meli, M. Peruzzini and F. Vizza, *Organometallics*, 1990, **9**, 226.
17 S. L. Bartley, S. N. Bernstein and K. R. Dunbar, *Inorg. Chim. Acta*, 1993, **213**, 213.
18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley & Sons, New York, 4th edn., 1986.
19 (*a*) T. S. Peng, C. H. Winter and J. A. Gladysz, *Inorg. Chem.*, 1994, **33**, 2534; (*b*) G. A. Stark, A. M. Arif and J. A. Gladysz, *Organometallics*, 1997, **16**, 2909.
20 (*a*) C. Diaz and A. Arancibia, *Inorg. Chim. Acta*, 1998, **269**, 246; (*b*) G. Barrado, G. A. Carriedo, C. D. Valenzuela and V. Riera, *Inorg. Chem.*, 1991, **30**, 4416; (*c*) P. C. Cagle, O. Meyer, K. Weickhardt, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1995, **117**, 11730; (*d*) C. A. Bignozzi, S. Roffia, C. Chiorboli, J. Davila, M. T. Indelli and F. Scandola, *Inorg. Chem.*, 1989, **28**, 4350.
21 W. M. Laidlaw, R. G. Denning, T. Verbiest, E. Chauchard, A. Persons, *Nature* (*London*), 1993, **363**, 58.
22 See for example: R. Argazzi, C. A. Bignozzi, T. A. Heimer, G. J. Meyer, *Inorg. Chem.*, 1997, **36**, 2 and references therein.
23 The cyanide toxicity has been recently associated with the formation of Fe—CN—Cu units interacting with cytochrome-*c*; see M. J. Scott, S. C. Lee and R. H. Holm, *Inorg. Chem.*, 1994, **33**, 4651.
24 R. J. Abraham and P. Loftus, *Proton and Carbon-13 NMR Spectroscopy*, Heyden, London, UK, 1978.
25 H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH, Weinheim, Germany, 2nd edn., 1993.
26 (*a*) L. Busetto, A. Palazzi and R. Ros, *Inorg. Chem.*, 1970, **9**, 2792; (*b*) H. Werner, W. Beck and H. Engelmann, *Inorg. Chimica Acta*, 1969, **3**, 332; (*c*) W. Rigby, P. M. Bailey, J. A. McCleverty and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1979, 371.
27 D. Bereman, *Inorg. Chem.*, 1972, **11**, 1149.
28 (*a*) R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *Inorg. Chim. Acta*, 1993, **204**, 63. (*b*) R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1993, 723.
29 (*a*) M. M. El-Etri and W. M. Scovell, *Inorg. Chem.*, 1990, **29**, 480; (*b*) R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, 1971 **6**, 407; (*c*) J. B. Melpolder and J. L. Burmeister, *Inorg. Chim. Acta*, 1981, **49**, 115; (*d*) J. L. Burmeister, H. J. Gysling and J. C. Lim, *J. Am. Chem. Soc.*, 1969, **91**, 44.
30 I. E. Maxwell, *Inorg. Chem.*, 1971, **10**, 1782.
31 S. W. Lin and A. F. Schreiner, *Inorg. Chim. Acta*, 1971, **5**, 290.
32 (*a*) R. Hübener, U. Abram and J. Strähle, *Inorg. Chim. Acta*, 1994, **224**, 193. (*b*) R. Hübener, U. Abram and J. Strähle, *Inorg. Chim. Acta*, 1994, **216**, 223; (*c*) R. Hübener, K. Ortner, J. Strähle and U. Abram, *Inorg. Chim. Acta*, 1996, **244**, 109.
33 O. Kohle, S. Ruiler and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 4779.
34 (*a*) G. J. Baird and S. G. Davies, *J. Organomet. Chem.*, 1984, **262**, 215; (*b*) C. Bianchini, F. Laschi, M. F. Ottaviani, M. Peruzzini, P. Zanello and F. Zanobini, *Organometallics*, 1989, **8**, 893; (*c*) G. B. Richter-Addo, D. A. Knight, M. A. Dewey, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1993, **115**, 11863.
35 (*a*) H. C. E. McFarlane and W. McFarlane, in *Multinuclear NMR*, ed. J. Mason, Plenum Press, New York, 1991; (*b*) M. Lardon, *J. Am. Chem. Soc.*, 1970, **92**, 5063.
36 A. M. Bond, R. Colton, D. G. Humphrey, P. J. Mahon, G. A. Snook, V. Tedesco and J. N. Walter, *Organometallics*, 1998, **17**, 2977.
37 J. R. Kirchoff, M. L. Allen, B. V. Cheesman, K. Okamoto, W. R. Heineman and E. Deutsch, *Inorg. Chim. Acta*, 1997, **262**, 195.
38 S. Castellano and A. A. Bothner–By, *J. Chem. Phys.*, 1964, **41**, 3863.
39 D. S. Stephenson, G. A. Binsch, *J. Magn. Reson.*, 1980, **37**, 395; D. S. Stephenson and G. A. Binsch, *J. Magn. Reson.*, 1980, **37**, 409.
40 P. Barbaro, C. Bianchini, F. Laschi, S. Midollini, S. Moneti, G. Scapacci, P. Zanello, *Inorg. Chem.*, 1994, **33**, 1622.

Paper 8/06683C