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Coordination and reduction of isocyanide ligands
 in hydrido-carbonyl rhenium cluster chemistry. Synthesis
 and characterization of the anion
 $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNR})]^-$ and of the formimidoyl derivative
 $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NR})(\text{PMe}_2\text{Ph})]^-$ ($\text{R} = \text{C}_6\text{H}_{11}$)

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Abstract

The reaction of the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]^-$ with cyclohexylisocyanide gives the novel unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$. By reaction of this species with dimethylphenylphosphine a saturated compound is obtained, $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$, containing a bridging formimidoyl ligand. Two isomers of this anion have been identified and the structure of one of them has been elucidated by X-ray analysis. The anion contains an isosceles triangle of Re atoms with two longer hydrogen-bridged edges [mean 3.255 Å] and one shorter edge [3.164(1) Å], doubly bridged by the formimidoyl ligand and the third hydride. The phosphine ligand is coordinated in the axial direction with respect to the Re_3 plane, with a Re–P bond length of 2.454(7) Å.

Introduction

The stoichiometric reduction of CO and CN triple bonds by organometallic hydrides is a process of much interest because of the potential use of such species as homogeneous catalysts and for an understanding of the involved catalytic mechanisms. Isocyanides (which show a close analogy to carbon monoxide) are particularly suitable reagents for such studies, and they have been investigated in many systems, including mononuclear, polynuclear and cluster species [1–5]. In particular, the reaction of RNC molecules with the unsaturated $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ species was shown by Adams and Golembeski [6] to involve initially the addition of the isocyanide to the cluster, and, in a second step, hydride migration, which depending on the reaction conditions takes place (i) to the C atom, giving a bridging

formimidoyl ($\text{HC}=\text{NR}$), or (ii) to the N atom, giving a bridging iminyl ($=\text{C}=\text{NHR}$) ligand, both processes representing the first step of the reductive hydrogenation of the CN bond. In rhenium hydrido-carbonyl chemistry, insertion of isocyanides into a Re-H bond, to give a bridging formimidoyl ($-\text{CH}=\text{NR}$) ligand, has been previously observed only in the reaction of RNC with the unsaturated dinuclear species $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ [7].

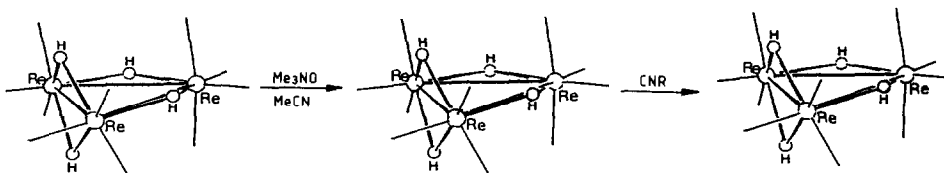
We have recently reported [8] that the reaction of the unsaturated anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ (**1**) [9] with Me_3NO , in the presence of a bielelectron donor molecule L (L = phosphines, pyridine or MeCN) results in substitution of one axial carbonyl of the $\text{Re}(\text{CO})_4$ vertex of **1** by the ligand L, to give $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9\text{L}]^-$ anions, which maintain the unsaturated $\text{Re}(\mu\text{-H})_2\text{Re}$ moiety present in **1**. The anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]^-$ (**2**), containing a labile acetonitrile ligand and four hydrides, seemed to us an appropriate choice for the reaction with RNC compounds, and we report here the results of these investigations, which led to the isolation and characterization of the anions $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ (**3**) and $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$ (two isomers, **4a** and **4b**). The results of a single crystal X-ray study of isomer **4b** as its NEt_4^+ salt are also reported.

Results and discussion

The reaction of **2** with one equivalent of cyclohexylisocyanide took place immediately at room temperature in CH_2Cl_2 , to give quantitatively the expected substitution product $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ (**3**). IR and ^1H NMR spectroscopy indicated that the product contained a terminally bonded isocyanide ($\nu(\text{CN})$ at 2187 cm^{-1}) and had retained the "unsaturated" $\text{Re}_3(\mu\text{-H})_4$ skeleton, of idealized C_s symmetry, present in the parent compounds **1** and **2**, which gives three hydridic resonances, in the ratio 1:1:2, the two at lower field (δ ca. -8) being attributable to the $\text{Re}(\mu\text{-H})_2\text{Re}$ moiety.

Compound **3** was also obtained directly from $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ by treatment with Me_3NO in the presence of the isocyanide, but the reaction was quite slow (ca. 18 h) and the product was contaminated by some unidentified by-products. The other synthesis is thus to be preferred.

In **3**, the isocyanide is terminally bound to a rhenium atom, which also bears hydrido ligands. However, no migration of a hydride from the cluster to the C atom of the isocyanide was observed; compound **3** is quite stable in solution under N_2 at room temperature for days, and no reaction occurs when a solution of **3** in THF was refluxed for several hours. Similar behaviour was shown by the related compound **2**, which contains acetonitrile, indicating that under these conditions, the hydrides are



Scheme 1.

unable to attack the CN triple bond, in contrast with their behaviour toward CO double bonds (formyl [10], acetone [11]), which are hydrogenated.

In the case of the previously reported [10] stepwise reduction of a carbonyl ligand of compound **1** to methanol, the hydrogenated carbon monoxide occupied the same coordination site as the isocyanide in **3**. The first step in the hydrogenation occurred upon treatment of **1** with $\text{Li}[\text{BH}(\text{s-Bu})_3]$, to give a formyl intermediate, which is unstable because of the fast migration of one hydride from the cluster to the carbon atom, leading to the stable complex $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{-CH}_2\text{O})(\text{CO})_9]^{2-}$. In the present case, however, no reaction was observed upon treatment of **3** with $\text{Li}[\text{BH}(\text{s-Bu})_3]$, at room temperature, indicating a much lower susceptibility toward nucleophilic attack on the carbon atom of the isocyanide.

In view of the fact that (i) in mononuclear hydrido-isocyanide complexes, the hydride insertion is promoted by the coordination of another ligand [2,3], which compensates the metal atom for the loss of two electrons associated with the transfer process, and (ii) compound **3** is formally an unsaturated species (46 valence electrons), we decided to examine some potential addition reactions. However, when CO was bubbled for some days through a solution of **3** no appreciable reaction was observed. By contrast, treatment of compound **3** in CH_2Cl_2 at room temperature with a stoichiometric amount of a tertiary phosphine with good donor properties, such as PMe_2Ph , resulted in an immediate reaction, which went to completion in ca. 1 h. The reaction was monitored by NMR spectroscopy, which revealed the formation of two isomers, **4a** and **4b**, each exhibiting three high field hydridic resonances, and a signal at δ ca. 10 characteristic of the hydrogen of the formimidoyl ligand -C(H)NR . The ratio **4a**/**4b** varied with time: at the beginning of the reaction both species were present, with **4a** slightly dominant. After ca. 1 h, when **3** had completely disappeared, they were present in about equimolar amounts, but when the mixture was kept overnight **4b** was the only species present.

An diffraction X-ray study (see below) of the crystals obtained from the reaction mixture revealed that they contained the anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$, with the phosphine axially coordinated to the Re atom not bearing the bridging formimidoyl, and *syn* with respect to this group (Fig. 1). The NMR spectrum of crystals identical to those used for the X-ray study confirmed that the structurally characterized species was **4b**.

Some information on the structure of **4a** was provided by the NMR spectra, which are quite similar for the two isomers. In particular, in both species two hydridic resonances are doublets (with $^2J(\text{H-P})$ in the range 10–20 Hz), while the third resonance is a broad unresolved triplet due to small couplings ($J < 2\text{Hz}$) with the phosphorus atom and with the formimidoyl hydrogen. This was confirmed by selective ^1H decoupling experiments. The broad hydridic resonances can therefore be attributed to the hydride bridging the Re–Re bond that is bridged by the formimidoyl group. This implies that in **4a** also the phosphine is bound to the rhenium atom not bearing the formimidoyl ligand, but with a different geometry (equatorial or axial *anti*). The values of $^2J(\text{H-P})$ could, in principle, aid in the structural assignment, because an equatorial coordination would imply the presence of both *cis* and *trans* $^2J(\text{H-P})$, which are usually quite different. In rhenium hydrido-carbonyl clusters *trans* $^2J(\text{H-P})$ couplings have always been found to be smaller than the *cis* couplings (in particular, for complexes with PMe_2Ph , the ranges are 0–6 Hz for *J trans* and 13–19 Hz for *J cis* [12]). Indeed, in **4a** one $^2J(\text{H-P})$

coupling constant (10 Hz) is smaller than the other (15 Hz), as expected for a *J trans* with respect to a *J cis* coupling, but its value is half way between the two ranges, and so we cannot establish unambiguously the structure of **4a**. We think, however, that the presence of only one isomer in addition to **4b** strongly suggests that the phosphine ligand in **4a** has an axial *anti* location to the formimidoyl ligand, since equatorial coordination would give rise to two different isomers of comparable stability.

If the phosphine in **4a** is assumed to have the axial *anti* location, the irreversible **4a**–**4b** isomerization suggests that the PMe_2Ph group has a lower steric interaction with the bridging formimidoyl ligand than with two carbonyls.

Description of the structure of **4b**

The structure of the anion **4b**, in its NEt_4^+ salt, is illustrated in Fig. 1, and bond distances and angles are listed in Table 1. The anion contains an isosceles Re_3 triangle, with two longer metal-metal edges, which are assumed to be hydrogen-bridged [Re1-Re2 3.280(1), Re1-Re3 3.229(1) Å], and one shorter edge [Re2-Re3 3.164(1) Å], which is doubly bridged by the formimidoyl ligand and the third hydride. The Re–Re bond lengths are comparable with those found in other triangular rhenium clusters containing a $\mu\text{-}\eta^2$ -ligand, e.g. in [$\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-OC(Ph)NH})^-$] [mean of the two longer Re–Re bonds 3.281 Å; shorter edge 3.153(2) Å] [13]. The phosphine ligand is bound to Re1 [Re1-P 2.454(7) Å] in the axial direction, on the side of the Re_3 plane occupied by the formimidoyl group.

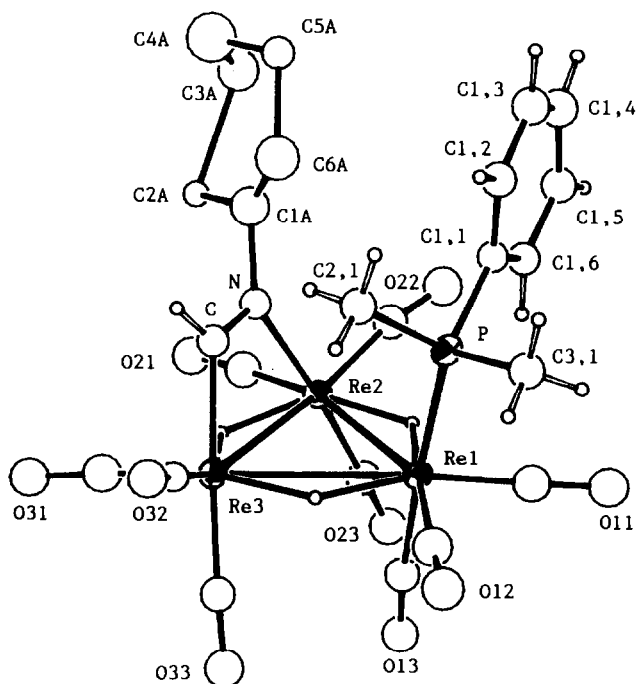


Fig. 1. A view of the anion [$\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})^-$] (**4b**). For clarity only one of the two models of disorder for the cyclohexyl group is depicted.

Table 1

Bond distances (Å) and angles (deg) in the anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H) = NC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$ (4b)

<i>Distances</i>			
Re1–Re2	3.280(1)	N–C	1.29(3)
Re1–Re3	3.229(1)	N–C1A	1.53(3)
Re2–Re3	3.164(1)	C11–O11	1.22(3)
Re1–P	2.454(7)	C12–O12	1.18(3)
Re1–C11	1.83(3)	C13–O13	1.12(3)
Re1–C12	1.88(3)	C21–O21	1.22(3)
Re1–C13	1.93(3)	C22–O22	1.15(3)
Re2–C21	1.84(3)	C23–O23	1.13(3)
Re2–C22	1.86(3)	C31–O31	1.20(3)
Re2–C23	1.95(3)	C32–O32	1.17(2)
Re2–N	2.19(2)	C33–O33	1.19(3)
Re3–C31	1.84(3)		
Re3–C32	1.90(3)	P–C1,1	1.84(2)
Re3–C33	1.90(3)	P–C2,1	1.84(3)
Re3–C	2.13(2)	P–C3,1	1.84(3)
<i>Angles</i>			
Re2–Re1–C11	108.9(9)	Re1–Re3–C31	163.3(9)
Re2–Re1–C12	155.7(9)	Re1–Re3–C32	104.4(7)
Re2–Re1–C13	80.0(7)	Re1–Re3–C33	86.8(8)
Re2–Re1–P	102.1(1)	Re1–Re3–C	91.2(7)
Re3–Re1–C11	163.6(9)	Re2–Re3–C31	103.2(9)
Re3–Re1–C12	99.0(9)	Re2–Re3–C32	152.2(7)
Re3–Re1–C13	81.2(8)	Re2–Re3–C33	113.4(8)
Re3–Re1–P	101.6(2)	Re2–Re3–C	64.0(7)
C11–Re1–C12	92(1)	C31–Re3–C32	92(1)
C11–Re1–C13	87(1)	C31–Re3–C33	93(1)
C11–Re1–P	90.8(9)	C31–Re3–C	88(1)
C12–Re1–C13	89(1)	C32–Re3–C33	88(1)
C12–Re1–P	90.0(9)	C32–Re3–C	94.2(9)
C13–Re1–P	177.1(8)	C33–Re3–C	177(1)
Re1–Re1–C21	165.4(8)	Re1–C11–O11	174(3)
Re1–Re2–C22	107.9(8)	Re1–C12–O12	176(3)
Re1–Re2–C23	89.9(8)	Re1–C13–O13	173(2)
Re1–Re2–N	89.7(5)	Re2–C21–O21	176(2)
Re3–Re2–C21	107.0(9)	Re2–C22–O22	171(2)
Re3–Re2–C22	158.1(9)	Re2–C23–O23	177(3)
Re3–Re2–C23	111.3(8)	Re3–C31–O31	173(3)
Re3–Re2–N	64.4(5)	Re3–C32–O32	178(2)
C21–Re2–C22	87(1)	Re3–C33–O33	172(2)
C21–Re2–C23	89(1)	Re2–N–C	113(2)
C21–Re2–N	90(1)	Re2–N–C1A	127(2)
C22–Re2–C23	85(1)	Re3–C–N	119(2)
C22–Re2–N	99(1)	C–N–C1A	120(2)
C23–Re2–N	157(1)		

The bond parameters involving the formimidoyl ligand are: Re3–C 2.13(2), Re2–N 2.19(2), C–N 1.29(3), N–C1A 1.53(3) Å, Re3–C–N 119(2), Re2–N–C 113(2), Re2–N–C1A 127(2), C–N–C1A 120(2)°. The values are comparable with those observed for similar interactions; in particular the Os–C, Os–N, C–N,

Os–C–N and Os–N–C bond parameters in $\text{Os}_3(\mu\text{-H})(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NC}_6\text{H}_5)\{\text{P(OMe)}_3\}$ [6], the only $\mu\text{-}\eta^2$ -formimidoyl species previously structurally characterized, are 2.075(9), 2.150(6), 1.320(10) Å, 116.0(6) and 109.8(6)°, respectively. The dihedral angle between the planes (Re1, Re2, Re3) and (Re2, Re3, N, C) is 106.1°. The three axial carbonyl ligands on average have longer Re–C bonds (mean 1.93 Å) than the six equatorial ones (mean 1.86 Å).

Experimental

The reactions were performed under N_2 , in solvents deoxygenated and dried by standard methods. The IR spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer, and the NMR spectra on a Bruker WP 80 spectrometer. $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]$ was prepared as previously described [9]. $\text{C}_6\text{H}_{11}\text{CN}$ (Merck-Schuchardt) and $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)$ (Aldrich) were used as received.

Synthesis of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_4(\text{CNC}_6\text{H}_{11})(\text{CO})_9]$ (3)

(a) A solution of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]$ (22 mg, 0.0226 mmol) in MeCN was treated at room temperature with 1.8 mg (0.0245 mmol) of anhydrous Me_3NO . After 1 h, when IR monitoring showed that **1** had been completely converted into $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})]^-$, the solvent was removed under vacuum, and the residue (after two cycles of dissolution in CH_2Cl_2 and evaporation, to remove completely the NMe_3) was treated, in CH_2Cl_2 , with 3 μl (0.024 mmol) of $\text{CNC}_6\text{H}_{11}$. IR monitoring showed the immediate formation of **3**, which was isolated as a yellow solid by precipitation with n-heptane and purified by three cycles of dissolution and precipitation (18 mg, 0.017 mmol, 75% isolated yield). IR (THF) $\nu(\text{CN})$ 2187w, $\nu(\text{CO})$ 2034m, 2009s, 1998vs, 1938ms, 1910s cm^{-1} . ^1H NMR of the anion (CD_2Cl_2): 3.7 (s br, 1, NCH), 1.6–1.2 (m, 10, CH_2), –8.36 (s, 1, ReH), –8.48 (s, 1, ReH), –12.86 (s, 2, ReH). The resonances of the cyclohexyl group extensively overlap with that of the cationic methyl group. M.p. 115°C. (Found: C, 27.21; H, 3.06; N, 2.72. $\text{C}_{24}\text{H}_{35}\text{O}_9\text{N}_2\text{Re}_3$ calcd: C, 27.32; H, 3.32; N, 2.66%).

(b) A solution of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]$ (30 mg, 0.0308 mmol) in CH_2Cl_2 , was treated at room temperature with 4 μl (0.032 mmol) of $\text{CNC}_6\text{H}_{11}$ and 2.5 mg (0.033 mmol) of anhydrous Me_3NO . After 18 h spectroscopic monitoring showed the presence in solution of mainly **3**, accompanied by some unchanged **1** and small amounts of other unidentified products.

Reaction of $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]^-$ with PMe_2Ph

A solution of $[\text{NEt}_4][\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{CNC}_6\text{H}_{11})]$ (**3**) (31 mg, 0.0294 mmol) in CD_2Cl_2 in a NMR tube was treated with 4.5 μl (0.03 mmol) of PMe_2Ph . The progress of the reaction (at 295 K) was monitored by ^1H NMR spectroscopy, which revealed the disappearance of **3** in ca. 1 h and the formation of two species **4a** and **4b**: **4a** δ 10.5 (d, $J(\text{HH})$ 1.7 Hz, 1, CHNR), 7.9–7.3 (m, 5, PPh), 2.11 (s, br, 1, NCH), 1.94 (d, $J(\text{HP})$ 8 Hz, 3, PCH_3), 1.91 (d, $J(\text{HP})$ 8 Hz, 3, PCH_3), 1.6–0.9 (m, 10, C_6H_{11}), –12.9 (s broad, unresolved H–H and H–P couplings with $J < 2$ Hz, 1, ReH), –13.5 (d, $J(\text{HP})$ 10 Hz, 1, ReH), –14.6 (d, $J(\text{HP})$ 15 Hz, 1, ReH); **4b** δ 10.1 (s, 1, CHNR), 7.9–7.3 (m, 5, PPh), 2.07 (s, 1, NCH), 1.86 (d, $J(\text{HP})$ 8 Hz, 3, PCH_3), 1.84 (d, $J(\text{HP})$ 8 Hz, 3, PCH_3), 1.55–0.94 (m, 10, C_6H_{11}), –12.1 (d, $J(\text{HP})$ 18 Hz, 1, ReH), –13.1 (broad, unresolved H–H and H–P couplings with $J < 2$ Hz,

Table 2. Positional parameters and their estimated standard deviations for the anion $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C(H)=NC}_6\text{H}_{11})(\text{PMe}_2\text{Ph})]^-$ (**4b**).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Re1	0.36455(5)	0.13565(8)	0.18286(6)	4.55(2) ^a
Re2	0.18774(5)	0.21270(8)	0.17499(6)	4.73(2) ^a
Re3	0.32532(5)	0.37100(8)	0.19181(6)	5.07(3) ^a
O11	0.380(1)	−0.092(1)	0.201(1)	9.3(5)
O12	0.546(1)	0.150(2)	0.219(1)	9.8(6)
O13	0.4083(9)	0.141(1)	0.365(1)	7.9(5)
O21	0.052(1)	0.333(1)	0.195(1)	8.7(5)
O22	0.074(1)	0.039(1)	0.107(1)	9.2(5)
O23	0.221(1)	0.111(1)	0.338(1)	8.3(5)
O31	0.264(1)	0.572(1)	0.223(1)	9.2(5)
O32	0.437(1)	0.481(1)	0.126(1)	8.7(5)
O33	0.461(1)	0.367(1)	0.364(1)	9.0(5)
C11	0.371(1)	−0.001(2)	0.197(2)	8.1(8)
C12	0.477(2)	0.145(2)	0.208(2)	8.5(8)
C13	0.389(1)	0.144(2)	0.297(1)	7.0(7)
C21	0.105(1)	0.282(2)	0.186(2)	8.0(7)
C22	0.112(1)	0.110(2)	0.129(2)	7.4(7)
C23	0.209(1)	0.146(2)	0.278(2)	7.6(7)
C31	0.283(2)	0.490(2)	0.209(2)	8.9(8)
C32	0.395(1)	0.438(2)	0.152(1)	5.3(6)
C33	0.413(1)	0.372(2)	0.296(1)	6.9(6)
N	0.169(1)	0.299(1)	0.065(1)	5.7(5)
C	0.226(1)	0.364(2)	0.076(1)	5.8(6)
C1A	0.093(2)	0.298(2)	−0.014(2)	9.1(8)
C2A	0.019(2)	0.343(3)	0.005(2)	3.5(9)
C3A	−0.070(3)	0.281(5)	−0.101(4)	10(2)
C4A	−0.050(2)	0.326(3)	−0.152(2)	15(1)
C5A	0.011(3)	0.262(4)	−0.161(3)	7(1)
C6A	0.100(4)	0.275(5)	−0.077(4)	11(2)
C2B	0.047(3)	0.397(4)	−0.022(3)	8(1)
C3B	−0.042(3)	0.388(4)	−0.095(3)	6(1)
C5B	−0.011(2)	0.204(3)	−0.138(2)	5(1)
C6B	0.067(2)	0.206(4)	−0.052(3)	5(1)
P	0.3370(3)	0.1162(5)	0.0387(4)	5.1(2) ^a
C1,1	0.245(1)	0.045(2)	−0.024(1)	5.7(6)
C1,2	0.226(1)	0.047(2)	−0.107(1)	6.8(7)
C1,3	0.154(1)	−0.004(2)	−0.160(2)	8.2(8)
C1,4	0.107(2)	−0.055(2)	−0.130(2)	8.9(8)
C1,5	0.129(1)	−0.064(2)	−0.045(1)	7.3(7)
C1,6	0.200(1)	−0.009(2)	0.009(1)	6.0(6)
C2,1	0.333(1)	0.231(2)	−0.020(1)	6.9(7)
C3,1	0.418(1)	0.045(2)	0.024(1)	6.8(7)
NCT	0.704(1)	0.175(1)	0.575(1)	6.5(5)
CT1	0.683(2)	0.257(2)	0.511(2)	10(1)
CT2	0.731(2)	0.228(3)	0.656(2)	11(1)
CT3	0.765(2)	0.102(3)	0.565(2)	11(1)
CT4	0.634(2)	0.100(2)	0.559(2)	8.6(8)
CT5	0.653(2)	0.220(3)	0.422(2)	14(1)
CT6	0.764(2)	0.142(3)	0.729(2)	16(1)
CT7	0.848(2)	0.155(3)	0.582(2)	15(1)
CT8	0.560(2)	0.160(3)	0.565(2)	13(1)
H1	0.2616	0.1166	0.1752	—
H2	0.3900	0.2645	0.1904	—
H3	0.2255	0.3358	0.1830	—

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{1}{3} [a^2 \cdot B_{1,1} + b^2 \cdot B_{2,2} + c^2 \cdot B_{3,3} + ab(\cos \gamma) \cdot B_{1,2} + ac(\cos \beta) \cdot B_{1,3} + bc(\cos \alpha) \cdot B_{2,3}]$

1, ReH), -13.9 (d, $J(\text{HP})$ 19 Hz, 1, ReH). The isomer **4a** was slowly converted into **4b**, the ratio **4a**/**4b** decreasing during the reaction: it was 1.4 at ca. 60% of conversion of **3** (10 min), 1.0 at ca. 95% of conversion (ca. 45 min), and 0.4 after ca. 2.5 h. After the solution had been kept overnight, only **4b** was present. The solution was evaporated to dryness and crystals of **4b** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution. IR ($\nu(\text{CO})$, CH_2Cl_2) 2026ms, 1995s, 1987vs, 1926ms, 1897vs, 1880sh cm^{-1} . M.p. 140°C . (Found: C, 32.28; H, 3.93; N, 2.27. $\text{C}_{32}\text{H}_{46}\text{N}_2\text{O}_9\text{PRe}_3$ calcd: C, 32.21; H, 3.86; N, 2.35%).

X-Ray analysis

Crystal data. $\text{C}_{32}\text{H}_{46}\text{N}_2\text{O}_9\text{PRe}_3$, $M = 1192.3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 17.930(3)$, $b = 13.309(4)$, $c = 18.030(3)$ Å, $\beta = 113.86(1)^\circ$, $U = 3934.8$ Å³, $Z = 4$, $D_c = 2.013$ g cm^{-3} , $F(000) = 2256$, Mo- K_α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-}K_\alpha) = 94.21$ cm^{-1} .

Intensity measurements. The crystal sample was a small needle shaped prism of dimensions $0.05 \times 0.05 \times 0.20$ mm. It was mounted on a glass fibre in the air. Data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite monochromatized Mo- K_α radiation. The collection was performed by the ω -scan method within the limits $6^\circ < 2\theta < 50^\circ$. A variable scan-speed (from 2 to $20^\circ/\text{min}$) and a variable scan-range of $(0.8 + 0.35 \tan \theta)^\circ$ were used, with a 25% extension at each end of the scan-range for background determination. The total number of data collected was 7737. Three standard intense reflections, monitored every two hours, showed some crystal decay, which amount to ca. 20% at the end of the collection. The intensities were corrected for Lorentz, polarization, and decay effects. An empirical absorption correction was applied to the data, based on ψ -scans (ψ 0 – 360° every 10°) of suitable reflections with χ values close to 90° ; the relative transmission factors had values in the range 1.00–0.95. A total of 2142 significant [$I > 3\sigma(I)$] independent reflections was used in the structure solution and refinements.

Structure solution and refinements. All computations were performed on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

The structure was solved by Patterson and Fourier methods, which revealed the locations of all the non-hydrogen atoms. The cyclohexyl group of the isocyanide ligand was found to be disordered; the disorder was interpreted in terms of two models with equal occupancy, rotated by ca. 50° with respect to one another about the axis passing through the carbon atoms 1 and 4, and having these atoms in common. The bond parameters associated with these models were widely scattered and subject to high uncertainties. The refinements were carried out by full-matrix least-squares. Only the Re and P atoms were treated anisotropically. The hydrogen atoms were not included in the refinements. The bridging hydridic atoms were placed in calculated positions, with a mean Re–H bond length of 1.80 Å. The formimidoyl H atom and the phenyl hydrogens were also placed in ideal positions (C–H 0.95 Å). The final difference-Fourier map showed only some residual peaks, not exceeding ca. $1 \text{ e } \text{Å}^{-3}$, close to the metal atoms.

Weights were assigned according to the formula $w = 4F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{1/2}/L_p$ (I and L_p being the integrated intensity and the Lorentz-polarization correction, respectively); p was optimized to 0.05. The final values of the agreement indices R and R_w were 0.041 and 0.046, respectively (GOF = 1.140).

The atomic coordinates are reported in Table 2. The final list of observed and calculated structure factors and a table of thermal factors are available from the authors.

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