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Synthesis, characterisation and molecular structure of Re(III) 2-oxacyclocarbenes stabilised by a benzoyldiazenido ligand

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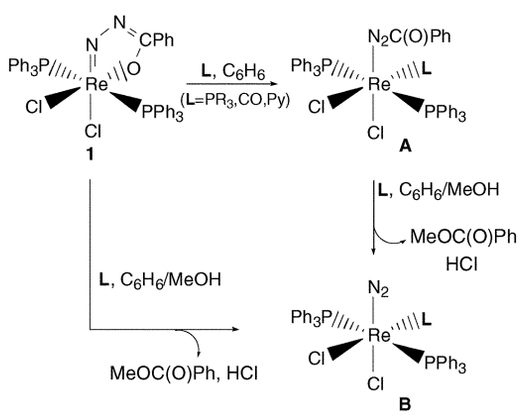
Received 3rd December 2003, Accepted 13th January 2004
First published as an Advance Article on the web 5th February 2004

A family of new Fischer-type rhenium(III) benzoyldiazenido-2-oxacyclocarbenes of formula [($ReCl_2\{\eta^1$-$N_2C(O)$-Ph$\}\{$=$C(CH_2)_nCH(R)O\}(PPh_3)_2$] [$n$ = 2, R = H (**2**), R = Me (**3**); n = 3, R = H (**4**), R = Me (**5**)] have been prepared by reaction of [$ReCl_2\{\eta^2$-$N_2C(Ph)O\}(PPh_3)_2$] (**1**) with ω-alkynols, such as 3-butyn-1-ol, 4-pentyn-1-ol, 4-pentyn-2-ol, 5-hexyn-2-ol in refluxing THF. The correct formulation of the carbene derivatives **2-5** has been unambiguously determined in solution by NMR analysis and confirmed for compounds **2**–**4** by X-ray diffraction methods in the solid state. All complexes are octahedral with the benzoyldiazenido ligand, Re$\{N_2C(O)Ph\}$, adopting a "*single bent*" conformation. The coordination basal plane is completed by an oxacyclocarbene ligand and two chlorine atoms. Two triphenylphosphines in *trans* positions with respect to each other complete the octahedral geometry around rhenium. The reactivity of **1** towards different alkynes and alkenes including propargyl- and allylamine has been also studied. With propargyl amine, monosubstituted or bisubstituted complexes, [($ReCl_2\{\eta^1$-$N_2C(O)Ph\}\{\eta^1$-NH_2-$CH_2C{\equiv}CH\}_n(PPh_3)_{3-n}$] [$n$ = 1 (**6**); n = 2 (**7**)], have been isolated depending on the reaction conditions. In contrast, the reaction with allylamine gave only the disubstituted complex [($ReCl_2\{\eta^1$-$N_2C(O)Ph\}\{\eta^1$-$NH_2CH_2CH{=}CH_2\}_2(PPh_3)$] (**8**). The molecular structure of the monosubstituted adduct **6** has been confirmed by X-ray analysis in the solid state.

Introduction

Fischer-type oxacyclocarbenes are a well known class of organometallic compounds which generally are obtained from the reaction of a variety of ω-alkynols with coordinatively unsaturated transition-metal ligand fragments.[1] Although most of these complexes contain metals of the chromium [1,2] and iron triad,[1,3] particularly ruthenium,[4] it has been seldom shown that oxacyclocarbenes may also be stabilised through coordination to manganese[5] and rhenium.[6] In particular, we have previously reported that the Dötz protocol for the synthesis of oxacyclocarbenes ligands may be successfully applied to the rhenium(I) complex [(triphos)$(CO)_2$Re(OTf)], which easily loses the weakly coordinated triflate ligand to generate the [(triphos)-$Re(CO)_2]^+$ synthon (triphos = $MeC(CH_2PPh_2)_3$).[7] The reaction of [(triphos)$(CO)_2$Re(OTf)] with different ω-alkynols is a straightforward process affording in excellent yield a variety of 2-oxacyclocarbene derivatives of formula [(triphos)$(CO)_2$-Re$\{$=$C(CH_2)_nCH(R)O\}]^+$ (n = 2, 3, 4; R = H, Me).[8,9] In these complexes the stabilisation of the oxacyclocarbene moiety is certainly favoured by the presence of the sterically demanding tripodal triphosphine, which provides the appropriate protective environment to accommodate the oxacyclocarbene ligand. The electron richness of the rhenium(I) centre may also contribute to stabilise this relatively unusual organometallic ligand. In this respect, it is worth mentioning that most of the known 2-oxacyclocarbenes, including those of chromium(0) or ruthenium(II), share with rhenium(I) the d^6 electronic-configuration. In order to verify if other ligands, less sterically demanding than triphos, may provide a suitable environment to stabilise rhenium(I) oxacyclocarbenes and investigate whether rhenium complexes in higher oxidation states may still form these type of carbenes, we have begun to study the reactivity of the benzoylhydrazido rhenium(V) complex [$ReCl_2\{\eta^2$-*N*,*O*-$N_2C(Ph)O\}(PPh_3)_2$] (**1**) towards ω-alkynols. Complex **1** is a versatile species for encompassing the two-step reduction, Re(V) ⟶ Re(III) ⟶ Re(I), involving a total of four electrons as was originally demonstrated by Chatt *et al*. (Scheme 1).[10]



Scheme 1

To better account for this redox process, it should be noted that the benzoylhydrazido ligand in **1** behaves as a hemilabile ligand allowing opening of the chelating ring upon reaction with a variety of nucleophiles. As a result, organodiazenido compounds of formula [$ReCl_2L\{\eta^1$-*N*-$N_2C(O)Ph\}(PPh_3)_2$] (L = neutral monodentate ligand such as PR_3, CO or pyridine) have been readily obtained (**A**).[11] A further two-electron reduction is generally feasible when the nucleophilic attack is carried out in MeOH. In the latter case, the reduction process is accompanied

DOI: 10.1039/b315693a

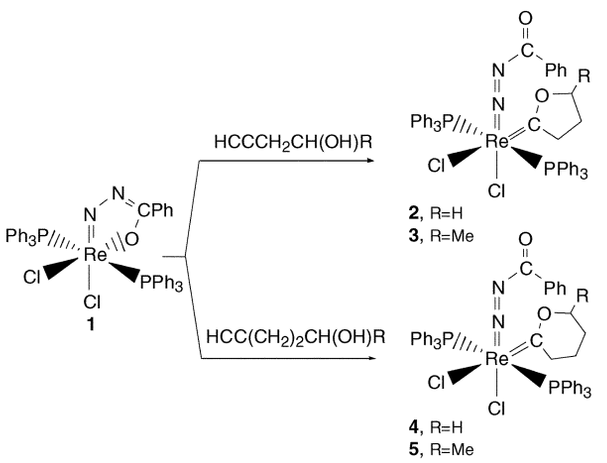
by the breakdown of the benzoylhydrazido moiety by releasing of methyl benzoate and hydrochloric acid whereas a side-on dinitrogen ligand is left on the rhenium to form $[ReCl_2(N_2)(L_2)(PPh_3)_2]$ complexes (**B**).[10]

In this paper we show that rhenium(III) oxacyclocarbene complexes may be synthesised starting from **1** and provide details on the synthesis, the NMR spectroscopic behaviour and the structural characterisation of $[ReCl_2\{\eta^1\text{-}N\text{-}N_2C(O)Ph\}\{=C(CH_2)_nCH(R)O\}(PPh_3)_2]$ [n = 1, R = H (**2**), R = Me (**3**); n = 2, R = H (**4**), R = Me (**5**)] complexes. The reaction of **1** with different alkynes and alkenes is also briefly discussed.

Results and discussion

Synthesis and characterisation of 2-oxacyclocarbene complexes

Reaction of a slight excess of the appropriate ω-alkynol, $HC{\equiv}C(CH_2)_nCH(R)OH$ (n = 1, 2; R = H, Me), with **1** in THF under reflux, affords, after η^2-*N*,*O*- to η^1-*N*-coordination slippage of the organodiazenido ligand, the 2-oxacyclocarbene rhenium complexes $[ReCl_2\{\eta^1\text{-}N\text{-}N_2C(O)Ph\}\{=C(CH_2)_nCH(R)O\}(PPh_3)_2]$ [n = 1, R = H (**2**), R = Me (**3**); n = 2, R = H (**4**), R = Me (**5**)] in fairly good yield (Scheme 2). Compounds **2**–**5** are obtained irrespectively of the reaction solvent (benzene, CH_2Cl_2, $CHCl_3$) and the reaction conditions (temperature and ratio between **1** and the ω-alkynol). Particularly, the presence of methanol, which is known to promote the elimination of methyl benzoate from benzoylhydrazido complexes, resulting in a metal coordinated dinitrogen species, does not affect the outcome of the reaction.[10]

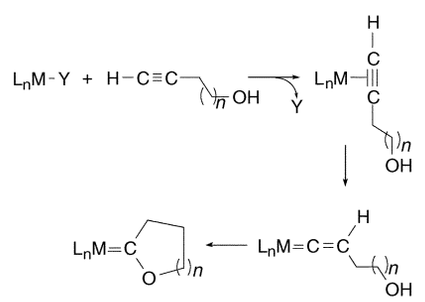


Scheme 2

Complexes **2**–**5** are orange, air-stable crystalline materials, which may be recrystallised in the air from CH_2Cl_2–EtOH mixtures. They have been characterised by elemental analyses and chemico-physical measurements including IR and NMR (^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$) spectroscopy. Table 1 summarises selected NMR data (see below) while IR data, other chemico-physical properties and elemental analysis are gathered in the Experimental section. In addition, the solid-state structure of **2**–**4** has been determined by X-ray diffraction methods (see below).

A remarkable structural feature shared by all the complexes **2**–**5** is the presence of a 2-oxacyclocarbene ligand *cis* disposed to a N-bonded benzoyldiazenido ligand which forms after oxygen detachment from rhenium and opening of the five-membered ring in **1**. In keeping with this structural rearrangement, inspection of the IR spectra of **2**–**5** shows two medium-to-strong intensity bands in the range 1648–1663 and 1537–1551 cm^{-1} assigned to ν(C=O) and ν(N=N) absorptions, respectively. These bands are typical of metal complexes bearing the η^1-*N*-$N_2C(O)Ph$ organodiazenido moiety, while a medium-intensity band around 1240 cm^{-1} indicates the presence of the benzoyl group.[11a,12] The latter is partially superimposed to an additional medium intensity band between 1220 and 1250 cm^{-1} ascribable to the ν(COC) absorption of the oxacyclic carbene ligand.[8,9] The NMR analysis of **2**–**5** in $CDCl_3$, show typical diamagnetic spectra confirming the presence of 2-oxacyclocarbene ligands. Unexpectedly, each NMR spectra are complicated by the occurrence of a dynamic equilibrium between two isomeric species which affects the solution behaviour of all of the oxacyclocarbene complexes here described (see below, NMR section). Particularly informative for validating the presence of a carbene ligand in either isomers is the typical low-field triplet resonance occurring at *ca.* 300 ppm (J_{CP} *ca.* 8 Hz) in the $^{13}C\{^1H\}$ NMR.[8] Attempts to separate the two isomers by TLC chromatography on either alumina or silica using different combinations of eluents (*n*-hexane, CH_2Cl_2, $CHCl_3$, CH_3CN) failed likely as a consequence of very similar R_f values.

In situ NMR monitoring of the reaction between **1** and typical alkynols, such as 3-butyn-1-ol and (±)-5-hexyn-2-ol, was attempted to clarify the mechanism leading to the 2-oxacyclocarbenes **2**–**5**. In contrast to our expectation, monitoring the alkynol addition to a cooled, deoxygenated, CD_2Cl_2 solution of **1** in a 5-mm NMR tube, does not provide any mechanistic information because of the complete lack of reactivity up to *ca.* 0 °C. At this temperature, a fast and unselective process takes place resulting in the rapid and simultaneous formation of a pair of isomers for both the ω-alkynols used for the NMR experiment. On the other hand, the absence of any intermediate does not represent a serious opposition to the hypothesis that the usual mechanism, which is generally assumed to drive the formation of 2-oxacyclocarbene species, is also responsible for the formation of **2**–**5** from **1** and the alkynol. The only necessary prerequisite is that a coordination vacancy is easily provided by rhenium and this is in fact the case for the present benzoylhydrazido complexes, which upon decoordination of the oxygen linkage, may readily generate an empty coordination site available to accommodate the alkynol molecule. From now on, the well-known sequential cascade entailing π-alkyne to hydroxyvinylidene tautomerization followed by intramolecular nucleophilic attack of the OH end to the electron deficient C_α carbon, may account well for the 2-oxacyclocarbene formation (Scheme 3).[8,13]



Scheme 3

Dynamic NMR properties of complexes 2–5

The solution behaviour of complexes **2**–**5** was examined in detail by NMR spectroscopy. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of complexes **2**–**5** were recorded at 294 K in both $C_2D_2Cl_4$ and $CDCl_3$ solutions. All resonances were unequivocally attributed on the basis of conventional 1D spectra, homo- ($^1H\{^1H\}$) and heteronuclear ($^1H\{^{31}P\}$) decoupling NMR experiments, 2D ^1H COSY, ^1H–^{13}C correlations and ^1H NOESY/ROESY spectra. The labelling scheme adopted for complexes **2**–**5** is shown in Fig. 1. As mentioned above, the NMR spectra show that at room temperature solutions of all complexes exist as a mixture of two isomers (A, major; B, minor; molar ratio, based on ^1H NMR integration, *ca.* 2.1 : 1 for **2**, 3.4 : 1 for **3**, 1.1 : 1 for **4**, 2.0 : 1 for **5**).

Table 1 Selected ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectral data for the complexes **2**–**5**

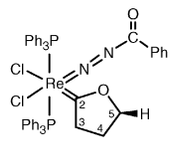
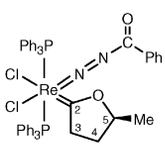
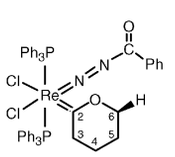
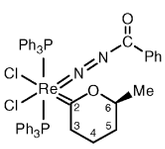
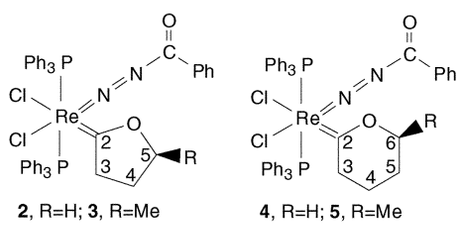
Complex	^{1}H [a] (δ, ppm; J, Hz)	$^{31}P\{^{1}H\}$ [b] (δ, ppm; J, Hz)	$^{13}C\{^{1}H\}$ [c] (δ, ppm; J, Hz)
2	Isomer A [d]		
	0.67, 2H, qnt, $^{3}J_{HH}$ = 8.0, $H_4\alpha$ 2.11, 2H, t, $^{3}J_{HH}$ = 7.9, $H_3\alpha$ 4.42, 2H, t, $^{3}J_{HH}$ = 8.0, $H_5\alpha$ 7.24, 2H, m, *m*-COPh 7.42, 1H, m, *p*-COPh 7.53, 2H, m, *o*-COPh	s, 0.44, 2P	298.07, t, $^{2}J_{CP}$ = 7.6, C_2 52.24, C_3 20.51, C_4 84.43, C_5 168.27, t, $^{4}J_{CP}$ = 3.5, CO
	Isomer B [d]		
	0.92, 2H, qnt, $^{3}J_{HH}$ = 8.0, $H_4\alpha$ 3.28, 2H, t, $^{3}J_{HH}$ = 7.9, $H_3\alpha$ 3.88, 2H, t, $^{3}J_{HH}$ = 7.7, $H_5\alpha$ 7.30,[f] 2H, m, *m*-COPh 7.50, 1H, m, *p*-COPh 7.64, 2H, m, *o*-COPh	s, 0.80, 2P	291.24, t, $^{2}J_{CP}$ = 7.6, C_2 169.34, t, $^{4}J_{CP}$ = 3.8, CO, 57.19, C_3 21.43, C_4 81.85, C_5
3	Isomer A [d]		
	0.23, 1H, dq, $^{2}J_{HH}$ = 12.0, $^{3}J_{HH5}$ = 9.5, $H_4\alpha$ 1.09, 1H, dddd, $^{3}J_{HH_s}$ = 7.4, $H_4\beta$ 1.27, 3H, d, Me 1.63, 1H, dtt, $^{3}J_{HH}$ = 10.0, $^{4}J_{HP}$ = 1.8, $H_3\beta$ 2.89, 1H, dddd, $^{2}J_{HH}$ = 20.3, $^{3}J_{H\alpha H\alpha}$ = 9.5, $^{3}J_{H\alpha H\beta}$ = 1.8, $^{4}J_{HP}$ = 1.0, $H_3\alpha$ 4.51, 1H, ddq, $^{3}J_{HH_{Me}}$ = 6.3, $H_5\alpha$ 7.27, 2H, m, *m*-COPh 7.46, 1H, m, *p*-COPh 7.56, 2H, m, *o*-COPh	0.53, $^{2}J_{PP}$ = 264.5, P_1,[e] 0.19, P_2 [e]	296.76, t, $^{2}J_{CP}$ = 8.6, C_2 52.74, C_3 28.54, C_4 91.26, C_5 20.70, Me t, 167.23, $^{4}J_{CP}$ = 3.1, CO
	Isomer B [d]		
	0.53, 1H, dddd, $^{2}J_{HH}$ = 12.0, $^{3}J_{HH_s}$ = 10.1, $H_4\alpha$ 1.05, 3H, d, Me 1.30,[f] 1H, $^{3}J_{HH_s}$ = 7.4, $H_4\beta$ 3.06, 1H, dddt, $^{3}J_{H\beta H\alpha}$ = 10.4, $^{3}J_{H\beta H\beta}$ = 9.2, $^{4}J_{HP}$ = 1.6, $H_3\beta$ 3.67, 1H, dddd, $^{2}J_{HH}$ = 19.6, $^{3}J_{H\alpha H\alpha}$ = 8.7, $^{3}J_{H\alpha H\beta}$ = 2.2, $^{4}J_{HP}$ = 1.0, $H_3\alpha$ 3.88, 1H, ddq, $^{3}J_{HH_{Me}}$ = 6.4, $H_5\alpha$ 7.32,[f] 2H 7.51, 1H, m, *p*-COPh 7.68, 2H, m, *o*-COPh	1.31, $^{2}J_{PP}$ = 270.6, P_1,[e] 0.04, P_2 [e]	290.42, t, $^{2}J_{CP}$ = 8.1, C_2 58.58, C_3 29.34, C_4 91.00, C_5 19.62, Me 168.12, t, $^{4}J_{CP}$ = 3.0, CO
4	Isomer A		
	3.33, 1H, t, $^{3}J_{HH}$ = 6.4, $H_3\alpha$ 0.87, 2H, qnt, $^{3}J_{HH}$ = 6.7 $H_4\alpha$ 0.95, 2H, qnt, $^{3}J_{HH}$ = 6.3, $H_5\alpha$ 3.83, 2H, t, $^{3}J_{HH}$ = 5.7, $H_6\alpha$ 7.55, 2H, m, *o*-COPh 7.48, 2H, m, *m*-COPh 7.31, 1H, m, *p*-COPh	s, 0.55, 2P	302.21, t, $^{2}J_{CP}$ = 8.3, C_2 50.88, C_3 17.38, C_4 20.80, C_5 73.38, C_6 167.92, t, $^{4}J_{CP}$ = 2.8, CO
	Isomer B		
	2.51, 2H, t, $^{3}J_{HH}$ = 6.5, $H_3\alpha$ 0.49, 2H, qnt, $^{3}J_{HH}$ = 6.5, $H_4\alpha$ 1.00, 2H, qnt, $^{3}J_{HH}$ = 6.4, $H_5\alpha$ 4.27, 2H, t, $^{3}J_{HH}$ = 5.9, $H_6\alpha$ 7.55–7.30, m, 5H COPh [g]	s, 0.07 (2P)	296.82, t, $^{2}J_{CP}$ = 8.3, C_2 44.89, C_3 16.54, C_4 21.09, C_5 73.87, C_6 167.11, t, $^{4}J_{CP}$ = 2.9, CO
5	Isomer A		
	2.12, 1H, dt, $^{2}J_{HH}$ = 19.4, $^{3}J_{HH}$ = 6.2, $H_3\alpha$ 2.89, 1H, dt, $^{2}J_{HH}$ = 19.6, $^{3}J_{HH}$ = 7.0, $H_3\beta$ 0.57,[f] 1H, $H_4\alpha$ 0.57,[f] 1H, $H_4\beta$ 1.36,[f] 1H, $^{3}J_{HH_a}$ = 2.9, $H_5\alpha$ 0.47,[f], 1H, $^{3}J_{HH_g}$ = 10.6, $H_5\beta$ 4.04, 1H, ddq, $^{3}J_{HH_{Me}}$ = 6.3, $H_6\alpha$ 1.30, 3H, d, Me 7.56, 2H, m, *o*-COPh 7.27, 2H, m, *m*-COPh 7.46, 1H, m, *p*-COPh	1.31,$^{2}J_{PP}$ = 268.5, P_1 0.12, P_2 [e, d]	302.85, t, $^{2}J_{CP}$ = 7.0, C_2 43.80, C_3 17.07, C_4 28.47, C_5 81.09, C_6 21.38, Me 167.13, t, $^{4}J_{CP}$ = 3.1, CO

Table 1 (*Contd.*)

Complex	^{1}H [a] (δ, ppm; J, Hz)	$^{31}P\{^{1}H\}$ [b] (δ, ppm; J, Hz)	$^{13}C\{^{1}H\}$ [c] (δ, ppm; J, Hz)
	Isomer B		
	2.86,[f] 1H, q, J_{HH} = 6.1, $H_3\alpha$	1.42, $^{2}J_{PP}$ = 270.1, P_1	297.71, t, $^{2}J_{CP}$ = 8.3, C_2
	3.67, 1H, q, J_{HH} = 6.1, $H_3\beta$	1.32, P_2	49.97, C_3
	1.12, 1H, m, $H_4\alpha$		17.45, C_4
	0.87, 1H, m, $H_4\beta$		27.77, C_5
	1.34,[f] 1H, $^{3}J_{HH_6}$ = 2.9, $H_5\alpha$		79.80, C_6
	0.45,[f] 1H, $^{3}J_{HH_6}$ = 10.1, $H_5\beta$		20.65, Me
	3.30, 1H, ddq, $^{3}J_{HH_{Me}}$ = 6.3, $H_6\alpha$		167.94, t, $^{4}J_{CP}$ = 3.1, CO
	1.16, 3H, d, Me		
	7.68, 2H, m, *o*-COPh		
	7.32,[f] 2H, *m*-COPh		
	7.51, 1H, m, *p*-COPh		

[a] 400.132 MHz, $C_2D_2Cl_4$, 294 K. [b] 202.46 MHz, $C_2D_2Cl_4$, 294 K. [c] 125.76 MHz, $C_2D_2Cl_4$, 294 K. Chemical shifts in ppm, coupling constants (J) in Hz. Legend: m, multiplet; d, doublet; t, triplet; q, quartet; qnt, quintet; the label α denotes the opposite side of the oxacarbene plane with respect to the methyl group; the label β refers to same side. [d] $CDCl_3$. [e] AB spin system. [f] Partially overlapped with other resonances. [g] Masked by the corresponding resonances of isomer A.



2, R=H; **3**, R=Me **4**, R=H; **5**, R=Me

Fig. 1 Sketch of the complexes **2**–**5** showing the numbering scheme adopted for NMR assignments.

Both isomers of complexes **2** and **4** show a single set of resonances for both of the phosphorus nuclei and the methylenic protons of the oxacarbene. The chemical equivalence of these nuclei indicates that a time-averaged symmetry element is present in the complexes on the NMR time scale. The only symmetry element consistent with the solid-state structure, and accounting for the observed NMR behaviour, is the coordination plane of the metal atom containing the chloride ligands and encompassing the oxametallacycle pseudo-plane as well the organodiazenido plane.

In contrast with **2** and **4**, NMR spectroscopy shows that complexes **3** and **5** do not adopt a similar symmetry likely as a consequence of the methyl substituent residing on the oxacyclocarbene ring. In keeping with the lack of a symmetry plane, the $^{31}P\{^{1}H\}$ NMR spectra of **3** and **5** display a tightly coupled AB spin system for each isomer, while a diastereotopic pair of methylenic resonances are observed for the oxametallacycle protons in the ^{1}H NMR spectra. $^{2}J_{PP}$ coupling constants range from 264.5 to 270.6 Hz, thus confirming a *trans* arrangement of the two triphenylphosphine ligands in all compounds.[14]

^{1}H NOESY spectroscopy shows that the A and B isomers attain a slow exchange motional regime in complexes **2**–**5**. This is clearly shown by the ^{1}H NOESY spectra of **2**–**5** in which a selective $Me^{A} \leftrightarrow Me^{B}$, $H_{3\alpha}{}^{A} \leftrightarrow H_{3\alpha}{}^{B}$, $H_{3\beta}{}^{A} \leftrightarrow H_{3\beta}{}^{B}$, $H_{4\alpha}{}^{A} \leftrightarrow H_{4\alpha}{}^{B}$, $H_{4\beta}{}^{A} \leftrightarrow H_{4\beta}{}^{B}$, *etc*. exchange pattern is observed. The labels α and β were used to define the protons on the opposite side and on the same side as the methyl group with respect to the oxacyclocarbene plane. A section of the ^{1}H NOESY spectrum of **2** showing relevant cross-peaks is reported in Fig. 2 as an example. Analogous results were obtained by ^{1}H ROESY spectroscopy.

The dynamic process responsible for this exchange equilibrium can be attributed to the existence of an isomerism involving the benzoylhydrazido group, similar to the well known amide isomerization.[15] A sketch of the two possible geometric isomers is reported in Fig. 3. At first glance, the alternative mechanism accounting for the isomerization in **2**–**5** *via* restricted rotation around the Re=C bond can be ruled out as very high energy barriers have been previously reported for this motion in comparable systems.[8,16]

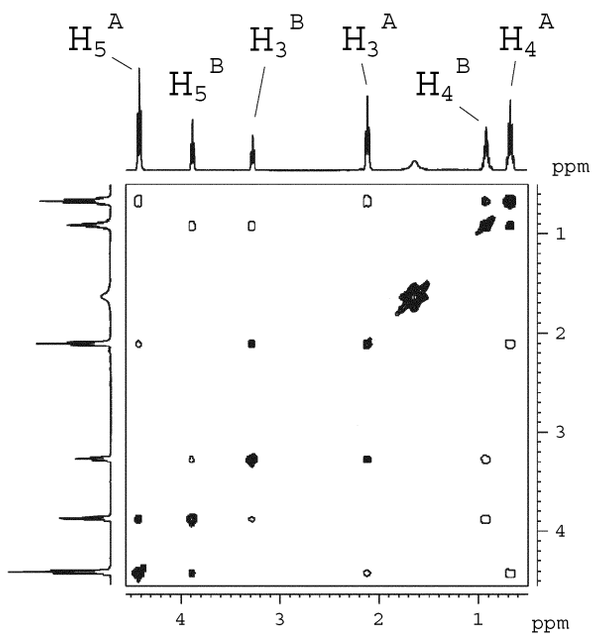


Fig. 2 Section of the ^{1}H NOESY spectrum of **2** ($CDCl_3$, 294 K, 400.13 MHz, τ_m = 0.65 s). Positive phased (exchange) cross-peaks are represented by filled circles, negative phased (NOE) cross-peaks are represented by empty circles.

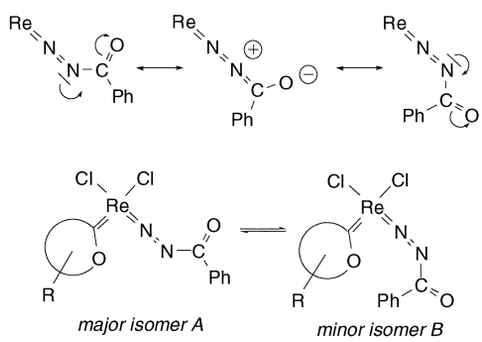


Fig. 3 Sketch of the geometric isomers of complexes **2**–**5**.

Consistently with the observed ^{1}H NOE interaction, the minor isomer B can be identified as the species destabilised by strong steric repulsions between the oxacyclocarbene and the organodiazenido groups (see Fig. 3). The measurement of activation parameters for the exchange process in complexes **2**–**5** are currently in progress on the basis of variable-temperature $^{31}P\{^{1}H\}$ NMR spectra and will be published in due course.

Structure and bonding of the oxacyclocarbene complexes

A relevant problem in all the compounds containing benzoylhydrazido ligands is the correct evaluation of the formal oxidation state of the metal centre. A perusal of the available literature on this class of compounds shows that the assignment of the metal oxidation state in complexes containing the organodiazenido ligand is not trivial. This group may exhibit different coordination modes entailing both linear *vs*. bent disposition of the –NNR unit as well as η^1- *vs*. η^2-hapticity when the residue R is bearing additional donor atoms.[17] Since crystallographic data have been largely used to assess the metal-oxidation state in this class of compounds,[18,19] it was decided to undertake a in-depth crystallographic study on the present family of rhenium 2-oxacyclocarbenes. Additionally, the collection of the X-ray data could be helpful to verify whether the occurrence of the solution equilibrium for the complexes **2**–**4** has an effect in the corresponding solid state structure.

X-Ray crystal structure analysis of the 2-oxacyclocarbene complexes 2, 3 and 4

ORTEP drawings showing the molecular structures of these complexes are given in Figs. 4–7. Pertinent crystallographic data are summarised in Table 2 while selected bond lengths and angles are listed in Table 3.

Crystals of **2** and **4** contain a solvent molecule of CH_2Cl_2 interspersed in the lattice per octahedral complex. For complex **3**, two type of crystals, namely **3a** and **3b**, were found within the same crystallization bulk. They are polymorphic crystals differing mainly by the colour, orange for **3a** and yellow for **3b**, and by the presence of a solvent molecule of ethanol in **3b**. In all derivatives studied by crystallographic methods, the rhenium atom has an octahedral environment with similar arrangements of the ligand set. The two triphenylphosphines are in *trans* position to each other and the basal plane is perpendicular to the P–Re–P vector and occupied by two *cis* chlorine atoms, the cyclic oxacarbene (2-oxacyclopentylidene in **2**, 2-oxa-3-methylcyclopentylidene in **3a** and **3b**, and 2-oxacyclohexylidene in **4**) and the monodentate organodiazenido(−) moiety. The short Re=N1 [ranging from 1.751(3) to 1.769(4) Å] and N1=N2 distances [in the range 1.222(6)–1.246(4) Å] as well as the linearity of Re=N1=N2 triatomic array [making angles from 170.3(5) to 174.4(3)°] are indicative of two adjacent Re=N=N double bonds. The structural data are in perfect agreement with those reported for other rhenium organodiazenido complexes.[20–27] The organodiazenido group is roughly planar and, for steric reasons, form angles of about 40° [39.4(1), 40.0(1), 39.3(1) and 39.9(1)° for **2**, **3a**, **3b** and **4**, respectively] with the mean basal plane passing through the Re, Cl1, Cl2, N1 and C8 atoms. The distances between Re and C8 of the oxacarbene rings are in the range of 1.990(4)–2.021(5) Å and well correspond to double bond distances Re=C as found in several rhenium carbenes authenticated by X-ray methods.[8,9,28,29] All the complexes show systematic lengthening of the Re–Cl1 distance with respect to the Re–Cl2 distance. Taking into account the average value for Re–Cl bond distance of 2.360(8) Å, determined from 15 structural determinations of $[ReCl_6]^{2-}$ complex ions,[30] the crystallographically meaningful difference affecting the distribution of the presently determined Re–Cl bond distances [Re–Cl1 from 2.506(2) to 2.516(1) Å and Re–Cl2 from 2.422(1) to 2.435(1) Å] can be accounted for in terms of a greater *trans* effect exerted by the cyclic oxacarbene group with respect to the organodiazenido moiety.

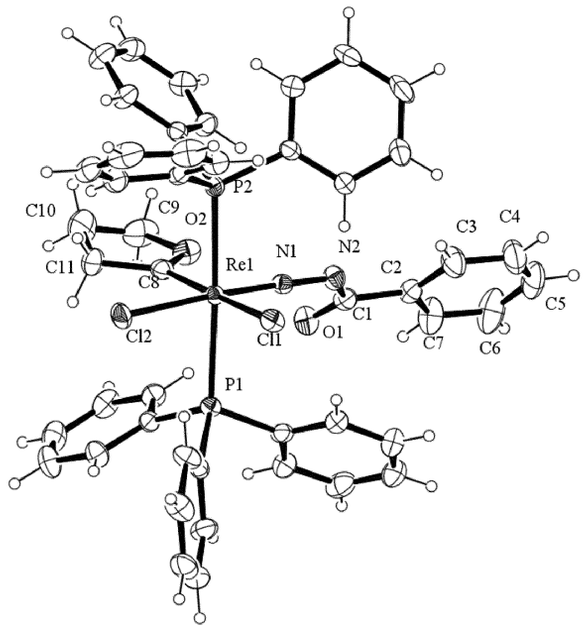


Fig. 4 An ORTEP view of complex **2** showing thermal ellipsoids at 30% probability.

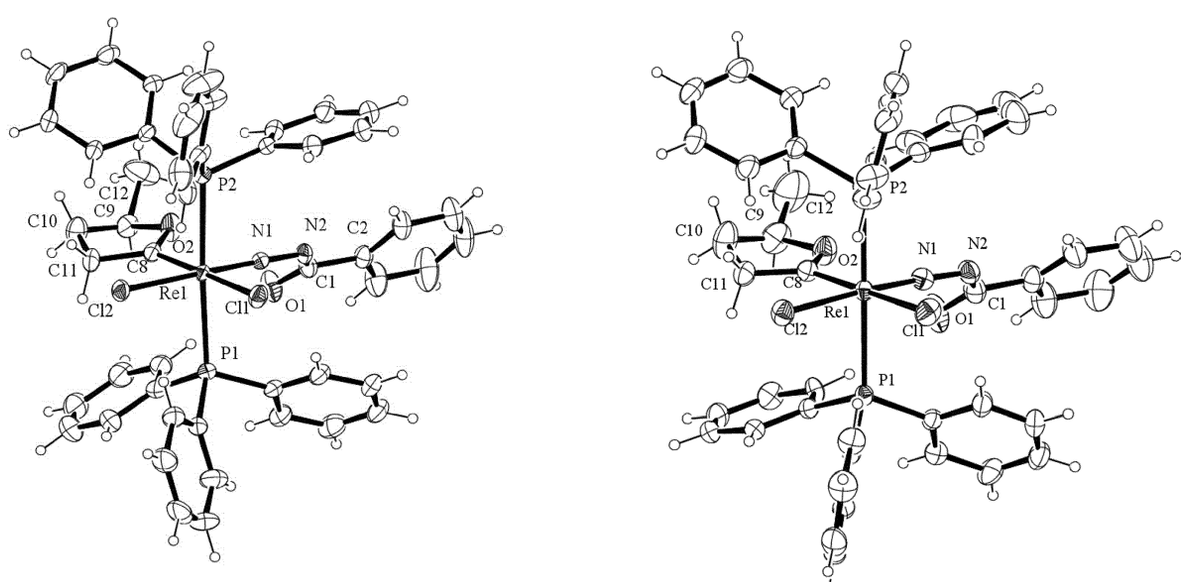


Fig. 5 ORTEP views of complexes **3a** (left) and **3b** (right) showing thermal ellipsoids at 30% probability. In compound **3a**, the C9(H)C12(H_2) moiety of the 2-oxa-3-methylcyclopentylidene ring, refined with two independent orientations, is shown only in one position for sake of clarity.

Table 2 Crystal data for complexes **2**–**4** and **6**

	2	**3a**	**3b**	**4**	**6**
Formula	$C_{47}H_{41}Cl_2N_2O_2P_2Re\cdot CH_2Cl_2$	$C_{48}H_{43}Cl_2N_2O_2P_2Re$	$C_{48}H_{43}Cl_2N_2O_2P_2Re\cdot C_2H_5OH$	$C_{48}H_{43}Cl_2N_2O_2P_2Re\cdot CH_2Cl_2$	$C_{46}H_{40}Cl_2N_3OP_2Re.\cdot CH_2Cl_2$
M	1069.78	999.88	1044.95	1083.81	1054.78
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$Pbcn$
a/Å	11.4338(2)	16.0911(2)	18.5316(3)	11.5556(2)	33.3037(1)
b/Å	25.3055(7)	15.0661(2)	11.9170(2)	25.2193(6)	11.0025(3)
c/Å	16.0016(4)	19.1572(3)	20.5233(4)	16.0768(2)	24.7218(5)
β/°	100.177(1)	110.089(1)	91.718(1)	101.176(1)	90
U/Å^3	4557.0(2)	4361.7(1)	4530.3(1)	4596.5(2)	9058.7(3)
Z	4	4	4	4	8
D_c/g cm^{-3}	1.559	1.521	1.532	1.566	1.547
T/K	295	295	295	295	295
μ/cm^{-1}	30.12	30.23	29.15	29.87	30.28
Range θ/°	2.6–28	3.5–28	3.6–28	2.4–28	2.7–28
Unique reflns.	10669	10503	10891	10977	10554
R_{int}	0.072	0.041	0.047	0.067	0.087
Observed reflns. [$I > 2\sigma(I)$]	7836	8175	8375	9096	7866
R (Obs. reflns.)	0.0441	0.0354	0.0505	0.0464	0.0491
wR (All reflns.)	0.0971	0.0857	0.1235	0.0981	0.1146
S	1.104	1.119	1.151	1.158	1.169
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	1.437, −1.108	1.583, −1.163	1.441, −1.449	1.545, −1.172	1.469, −0.951

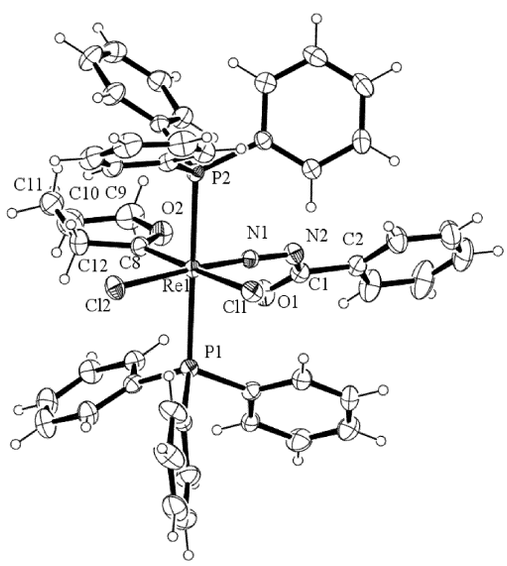


Fig. 6 An ORTEP view of complex **4** showing thermal ellipsoids at 30% probability. The C10(H_2)C11(H_2) moiety of the 2-oxacyclohexylidene ring, refined with two independent orientations, is shown only in one position for sake of clarity.

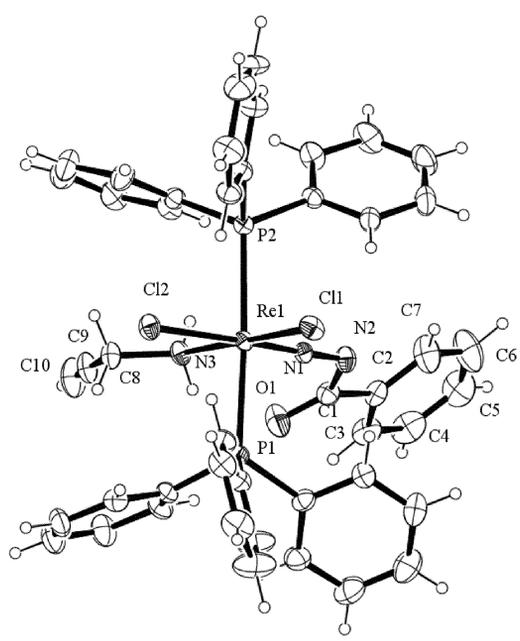


Fig. 7 An ORTEP view of complex **6** showing thermal ellipsoids at 30% probability.

The Re–P distances of the two *trans* triphenylphosphine ligands are in the range 2.484(1)–2.500(1) Å and are in agreement with other Re–P distances in rhenium(III) octahedral complexes.[31]

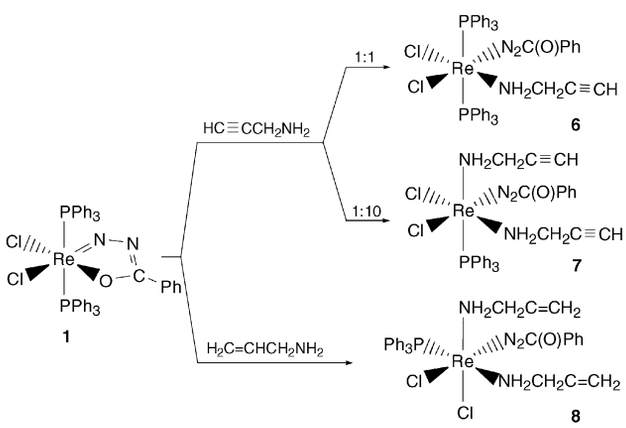
From inspection of the X-ray data and in agreement with the bent coordination mode displayed by the organodiazenido ligand, it seems plausible to assign a formal Re(III) oxidation state to the presented cyclic carbene complexes. Similar assignment was proposed by Chatt and Harman for related complexes[11a,32] and has been recently supported by X-ray studies carried out on some rhenium and technetium organodiazenido species.[22,29,33] In agreement with the presence of a rhenium(III) center, magnetic susceptibility measurements on **2** suggest the presence of two unpaired electrons with a μ_{eff} of 2.40 μ_B, at 21 °C. Similar values have been reported for other 5d^4 octahedral rhenium(III) systems.[34] At first glance, the paramagnetic solid state behaviour of **2** does not agree with the solution NMR spectra which are typical of diamagnetic complexes and consist of ^{1}H, ^{13}C and ^{31}P NMR spectra with narrow lines with chemical shifts within normal values.[35] However, this somewhat surprising behaviour has some precedents in the literature of Re(III)-d^4 complexes and has been interpreted either as a consequence of more or less severe distortions in solution of the octahedral symmetry[11a,19] or as a consequence of significant π-electron-transfer from ligand electrons to the t_{2g} orbitals of the metal ion.[33,36,37]

Reaction of 1 with other alkenes and alkynes

The successful reaction of **1** with ω-alkynols prompted us to preliminarily explore its reactivity with unsaturated hydrocarbons such as alkenes and alkynes. Selected substrates to investigate this chemistry were propargylic alcohols [HC≡CR_2-(OH), R = Me, Ph], mono- and di-substituted alkenes and alkynes [styrene, stilbene, RC=CR′ (R = H; R′ = Me, Ph; R = R′ = Ph)], and unsaturated amines such as propargylamine, HC≡CCH_2NH_2, and allylamine, H_2C=$CHCH_2NH_2$. Irrespectively, of the unsaturated substrate used, no reaction was obtained even under harsh reaction conditions (prolonged reflux in THF) and the starting material was recovered at the end of each reaction test. Only when propargylamine was reacted with **1**, a reaction took place with formation of a

Table 3 Selected bond distances (Å) and angles (°) for complexes **2**–**4**

	2	**3a**	**3b**	**4**
Re1–P1	2.494(1)	2.500(1)	2.492(1)	2.493(1)
Re1–P2	2.486(1)	2.484(1)	2.493(2)	2.484(1)
Re1–Cl1	2.509(1)	2.506(1)	2.507(2)	2.516(1)
Re1–Cl2	2.422(1)	2.435(1)	2.434(2)	2.425(1)
Re1–N1	1.752(4)	1.751(3)	1.755(5)	1.769(4)
Re1–C8	1.993(5)	1.990(4)	2.004(6)	2.021(5)
N1–N2	1.242(6)	1.246(4)	1.233(7)	1.222(6)
N2–C1	1.419(7)	1.399(5)	1.414(9)	1.406(7)
C1–O1	1.204(7)	1.209(5)	1.224(9)	1.208(6)
C8–O2	1.331(6)	1.326(5)	1.338(8)	1.325(6)
C8–C11	1.512(9)	1.514(6)	1.470(9)	
C8–C12				1.489(8)
P1–Re1–P2	174.01(5)	176.77(4)	178.88(5)	174.20(4)
P1–Re1–Cl1	90.43(4)	87.47(4)	89.38(5)	89.32(4)
P1–Re1–Cl2	85.06(5)	89.96(4)	86.37(5)	85.88(5)
P1–Re1–N1	91.7(1)	89.0(1)	90.3(2)	91.0(1)
P1–Re1–C8	93.5(2)	94.7(1)	93.2(2)	94.3(2)
P2–Re1–Cl1	85.73(4)	89.62(4)	89.95(5)	86.12(4)
P2–Re1–Cl2	90.12(5)	91.37(4)	92.72(5)	90.26(5)
P2–Re1–N1	93.1(1)	89.8(1)	90.6(2)	92.7(1)
P2–Re1–C8	89.9(2)	88.3(1)	87.4(2)	90.0(2)
Cl1–Re1–Cl2	86.89(5)	88.32(4)	87.60(6)	86.34(5)
Cl1–Re1–N1	93.4(1)	93.1(1)	92.3(1)	92.8(1)
Cl1–Re1–C8	173.3(2)	174.6(1)	174.6(2)	174.1(2)
Cl2–Re1–N1	176.8(1)	178.1(1)	176.7(2)	176.8(1)
Cl2–Re1–C8	88.0(2)	86.7(1)	87.9(2)	89.2(2)
N1–Re1–C8	92.0(2)	91.9(2)	92.3(2)	91.9(2)
Re1–N1–N2	172.4(4)	174.4(3)	170.3(5)	171.7(4)
Re1–C8–O2	121.3(4)	121.4(3)	121.5(4)	117.5(4)
Re1–C8–C11	130.4(4)	130.8(3)	131.3(4)	
Re1–C8–C12				125.9(4)
N1–N2–C1	120.7(4)	119.5(3)	119.4(5)	121.0(5)



Scheme 4

mixture of the mono- and bi-substituted complexes [($ReCl_2${η^1-$NH_2CH_2C{\equiv}CH$}$_n$(η^1-NNC(O)Ph)(PPh_3)$_2$] (n = 1 (**6**); n = 2 (**7**)) (Scheme 4). The composition of this mixture strictly depends on the stoichiometry between the amine and **1**. Particularly, when a tenfold excess of the amine was used, the yield of **7** increased by 70%, while, the monosubstituted derivative **6** was obtained as the main product only when a stoichiometric quantity of amine was added. Nonetheless, also in the 1 : 1 reaction, a variable amount of **7** (<10%) was observed by *in situ* NMR experiments. Fractional crystallization of mixtures enriched in each of the two amino-derivatives provided a good method to obtain a pure sample of each compound, albeit in moderate yield (<30% of pure compound).

Complexes **6** and **7** show elemental analysis, IR and NMR spectral data consistent with the assigned structures (see Experimental section). Slow crystallization from a dilute CH_2Cl_2–EtOH solution of a 9 : 1 mixture of **6** and **7** separated brownish microcrystals of **6** which were analytically pure and suitable for X-ray diffraction analysis. Crystallographic details

Table 4 Selected bond distances (Å) and angles (°) for complex **6**

Re1–P1	2.459(1)	N1–N2	1.260(6)
Re1–P2	2.460(1)	N2–C1	1.388(7)
Re1–Cl1	2.424(1)	C1–O1	1.227(8)
Re1–Cl2	2.416(2)	N3–C8	1.485(8)
Re1–N1	1.742(4)	C8–C9	1.489(8)
Re1–N3	2.222(4)	C9–C10	1.163(9)
P1–Re1–P2	174.42(4)	Cl1–Re1–Cl2	93.21(5)
P1–Re1–Cl1	87.67(5)	Cl1–Re1–N1	96.1(1)
P1–Re1–Cl2	87.69(4)	Cl1–Re1–N3	179.0(1)
P1–Re1–N1	92.3(2)	Cl2–Re1–N3	85.9(1)
P1–Re1–N3	91.9(1)	N1–Re1–N3	84.8(2)
P2–Re1–Cl1	90.13(5)	Re1–N1–N2	177.0(4)
P2–Re1–Cl2	87.31(5)	Re1–N3–C8	125.8(3)
P2–Re1–N1	93.0(2)		
P2–Re1–N3	90.2(1)		

are collected in Table 2. An ORTEP drawing is showing in Fig. 7 with selected bond distance and angles reported in Table 4. Crystals of **6** contain a solvent molecule of CH_2Cl_2 per octahedral complex which behaves as a genuine Re(III) derivative quite similar to complexes **2**–**4** described above, except for the propargylic amine ligand instead of a cyclic oxacarbene.

The diazenido group displays comparable metrical properties with those previously observed for complexes **2**–**4**, that is: Re=N1 and N1=N2 distances of 1.742(4) and 1.260(6) Å, respectively. In addition, its mean plane is rotated by an angle of 34.6(1)° with respect to the mean plane passing through the Re, N1, N3, Cl1 and Cl2 atoms. The Re–N3 (amine) bond length of 2.222(4) Å is typical for a single bond distance between Re and an amine nitrogen, while the short Re–Cl distances, 2.424(1) and 2.416(1) Å, indicate that both the propargylamino and benzoyldiazenido ligands exert a similar small *trans* effect on Cl atoms. The Re–P separations of the two mutually *trans* triphenylphosphine groups are very similar [2.459(1)–2.460(1) Å] and are in agreement with Re–P bond lengths found in the other four crystallographically studied rhenium(III) oxacyclocarbene octahedral complexes.[31]

As a final comment to this chemistry, it is notable that in complexes **6** and **7**, propargylamine coordinates to rhenium *via* the nitrogen atom, rather than with the alkyne triple bond. This behaviour does not appear surprising in view of the lack of reactivity of **1** with terminal alkynes and of the preference to coordinate *via* the N-donor atom shown by unsaturated amines towards rhenium.[38] In keeping with this result, it is found that treatment of **1** with $CH_2{=}CHCH_2NH_2$ in refluxing THF provides the coordinated *N*-allylamine complex [($ReCl_2$-{η^1-$NH_2CH_2CH{=}CH_2$}$_2$(η^1-NNC(O)Ph)(PPh_3)] (**8**) as a brown microcrystalline product obtained in low yield. The formulation of **8** as a bis-amino adduct derives from IR and NMR spectroscopy. Particularly, ^{1}H,^{1}H-2D NMR-COSY spectra helped to ascertain the presence of two *cis* coordinating inequivalent amines.

Finally, it is worth stressing that the chemical inertness shown by **1** towards terminal alkynes does not parallel the general reactivity shown by rhenium(I) complexes.[28] These latter, in fact, readily react with HCCR and propargylic alcohols to form stable vinylidene and allenylidene complexes, respectively.[28] This behaviour, although not representing any definitive proof, further supports the assigned +III oxidation state of rhenium in these organodiazenido derivatives. The reduced electron density at the d^4-metal centre, could be reasonably invoked to account for a better stabilization of carbenes in contrast to the more π-acid vinylidene ligands.

Conclusions

A series of rhenium(III) benzoyldiazenido-2-oxacyclocarbene complexes, namely [($ReCl_2${η^1-$N_2C(O)Ph$}{=$C(CH_2)_nCH(R)O$}-(PPh_3)$_2$] [n = 2, R = H (**2**), R = Me (**3**); n = 3, R = H (**4**), R = Me

(**5**)] have been synthesised. IR and NMR spectroscopy as well as single crystal X-ray studies, have shown that these complexes, representing the first documented examples of rhenium(III) oxacyclocarbene species, exhibit in both solid state and solution an octahedral geometry with a bent η^1-*N*-benzoyldiazenido ligand *cis* oriented with respect to the oxacyclocarbene unit.

Irrespectively of the oxacylocarbene ring size and substituents, the NMR analysis indicates the existence of an unprecedented dynamic behaviour where the two interconverting species probably exchange *via* an amide-like isomerization process involving the benzoyldiazenido moiety.

Experimental

General procedures

All reactions and manipulations were routinely performed under a dry nitrogen atmosphere by using standard Schlenk-tube techniques. Tetrahydrofuran (THF) was freshly distilled over $LiAlH_4$, *n*-hexane was stored over molecular sieves and purged with nitrogen prior to use, dichloromethane and methanol were purified by distillation over CaH_2 before use. All the other chemicals were reagent grade and unless otherwise stated were used as received from commercial suppliers without further purification. The purity of all alkynols (Aldrich) was checked by ^{1}H NMR spectroscopy and, when necessary, they were distilled under inert atmosphere prior to use. IR spectra were obtained in KBr using a Nicolet 510P FT-IR (4000–200 cm^{-1}) spectrophotometer. UV-Vis spectra were recorded with a LAMBQ 40 UV-VIS, Perkin–Elmer spectrophotometer. $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC200, Varian VXR300, or Bruker Avance DRX-400 spectrometers operating at 81.01, 121.42 and 161.98 MHz, respectively. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on the same instruments operating at 200.13, 299.94 and 400.13 MHz (^{1}H) and 50.32, 75.42 or 100.61 MHz (^{13}C), respectively. Chemical shifts are relative to tetramethylsilane as external reference or calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). ^{13}C-135 DEPT experiments were run on the Bruker AC200 spectrometer. Variable-temperature experiments were measured on the Bruker Avance DRX-400 spectrometer equipped with a variable-temperature control unit accurate to ±0.1 °C. The assignments of the signals resulted from 1D spectra, $^1H\{^{31}P\}$ heteronuclear decoupling experiments, ^{1}H COSY, ^{1}H-NOESY, ^{1}H-ROESY and proton detected ^{1}H,^{13}C and ^{1}H,^{31}P correlations using degassed nonspinning samples. 2D NMR spectra were recorded on the Bruker Avance DRX-400 instrument using pulse sequences suitable for phase-sensitive representations using TPPI. The ^{1}H,^{13}C and ^{1}H,^{31}P correlations [39] were recorded using an HMQC sequence with decoupling during acquisition. Standard pulse sequences were used for the ^{1}H-NOESY [40] and ^{1}H-ROESY [41] experiments with a 650 ms mixing time and 500 ms spin-lock time, respectively. Elemental analyses (C, H, N) were performed using a Carlo Erba model 1110 elemental analyser. MS-FAB spectra were acquired with a Hewlett-Packard MS ENGINE HP 5989A mass spectrometer (8 kV, 10 μA, probe temperature 50 °C), using nitrobenzyl alcohol as matrix. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 40 spectrophotometer. Magnetic measurements were carried out in the solid state with a magnetic susceptibility balance, MSB-AUTO, Sherwood Scientific Ltd, and in solution by the method of Evans in $CHCl_3$ purged with nitrogen.[35]

Synthesis of the complexes

[($ReCl_2$(η^2-*N*,*O*-NNC(O)Ph)(PPh_3)$_2$] (1). Complex **1** was prepared using a modification of the original method.[10*b*,11*a*,12] Solid benzoylhydrazine (2.9 g, 21.3 mmol) was added to a stirred suspension of $KReO_4$ (1.0 g, 3.4 mmol) in ethanol (60 mL) containing an excess of PPh_3 (4.7 g, 19.9 mmol) and 7 mL of concentrated HCl solution (84.5 mol). The emerald green solution was stirred at room temperature in the air for 30 min during which time **1** separated out as an emerald green powder. The solution was filtered out and the solid was washed with diethyl ether and dried under vacuum. Yield 84% (Found: C, 56.52; H, 3.90; N, 2.99. $C_{43}H_{35}Cl_2N_2OP_2Re$ requires C, 56.41; H, 3.86; N, 3.06%).

[$ReCl_2$(η^1-*N*-NNC(O)Ph){=C(CH_2)$_3$O}(PPh_3)$_2$] (2). A double proportion of 3-butyn-1-ol, HC≡C(CH_2)$_2$OH (33 μL, 0.44 mmol) was added *via* a syringe to a suspension of **1** (200 mg, 0.22 mmol) in THF (20 mL) and the temperature was slowly raised to the boiling point. After 3 h refluxing, the deep orange solution was concentrated under nitrogen to half volume. Addition of diethyl ether (3 mL) gave pale orange microcrystals of **2**, which were filtered off, washed with ethanol and diethyl ether and dried under vacuum. The crude solid was recrystallized from CH_2Cl_2–EtOH (1 : 2 v/v, 10 mL) to yield orange crystals suitable for X-ray diffraction analysis. Yield 85% (Found: C, 57.33; H, 4.24; N, 2.85. $C_{47}H_{41}Cl_2N_2O_2P_2Re$ requires C, 57.39; H, 4.19; N, 2.83%); ν_{max}/cm^{-1} 1650 $(CO)_{benzoyl}$, 1539 $(N{=}N)_{hydrazido}$, 1231 (COC_{ring}, benzoyl); UV-VIS (CH_2Cl_2) λ_{max1} = 287 nm (ε = 2099 M^{-1} cm^{-1}), λ_{max2} = 367 (522.4); FAB$^+$-MS: *m*/*z* 589 ($PPh_3Re(C_5H_6O)Cl_2^+$), 554 ($PPh_3Re(C_5H_6O)Cl^+$), 484 (PPh_3ReCl^+), 405 (PPh_2ReCl^+), 329 ($PPhReCl^+$).

[$ReCl_2$(η^1-*N*-NNC(O)Ph){=C(CH_2)$_2$CH(Me)O}(PPh_3)$_2$] (3). The methyl-substituted oxacyclocarbene complex **3**, was prepared as described above for **2** using (±)-4-pentyn-2-ol, HC≡CCH_2CH(OH)CH_3 (21 μL, 0.25 mmol) instead of 3-butyn-1-ol. Work-up as above, gave **3**, as orange microcrystals. Yield 83% (Found: C, 57.75; H, 4.38; N, 2.81. $C_{48}H_{43}Cl_2N_2O_2P_2Re$ requires C, 57.72; H, 4.34; N, 2.80%); ν_{max}/cm^{-1} 1663 $(CO)_{benzoyl}$, 1551 $(N{=}N)_{hydrazido}$, 1232 (COC_{ring} + COPh).

[$ReCl_2$(η^1-*N*-NNC(O)Ph){=C(CH_2)$_4$O}(PPh_3)$_2$] (4). The oxacyclocarbene complex **4**, was obtained as described above for **2** using 4-pentyn-1-ol (24 μL, 0.25 mmol) in place of 3-butyn-1-ol. Usual work-up gave **4** as pale orange crystals. Yield 86% (Found: C, 57.81; H, 4.37; N, 2.79. $C_{48}H_{43}Cl_2N_2O_2P_2Re$ requires C, 57.72; H, 4.34; N, 2.80%); ν_{max}/cm^{-1} 1648 $(CO)_{benzoyl}$, 1537 $(N{=}N)_{hydrazido}$, 1246 (COC_{ring}), 1222 (COPh).

[$ReCl_2$(η^1-*N*-NNC(O)Ph){=C(CH_2)$_3$CH(Me)O}(PPh_3)$_2$] (5). Replacing 3-butyn-1-ol with (±)-5-hexyn-2-ol, HC≡CCH_2-CH_2CH(Me)OH (48 μL, 0.25 mmol) in the above procedure gave orange microcrystals of **5**. Yield 80% (Found: C, 58.16; H, 4.50; N, 2.71. $C_{49}H_{45}Cl_2N_2O_2P_2Re$ requires C, 58.11; H, 4.48; N, 2.76%); ν_{max}/cm^{-1} 1650 $(CO)_{benzoyl}$, 1542 $(N{=}N)_{hydrazido}$, 1242 (COC_{ring}), 1222 (COPh).

***In situ* NMR monitoring of the reactions between 1 and 3-butyn-1-ol or (±)-5-hexyn-2-ol.** One equivalent of the appropriate alkynol (0.03 mmol of 3-butyn-1-ol or (±)-5-hexyn-2-ol) was added *via* syringe to a deoxygenated CD_2Cl_2 (0.8 mL) solution of **1** (25.0 mg, 0.03 mmol) in a 5 mm NMR, cooled at −78 °C with acetone/dry ice bath.

The tube was flame-sealed under nitrogen at −78 °C and introduced into the NMR probe of the spectrometer pre-cooled to −50 °C. The progress of the reaction was followed by recording $^{31}P\{^1H\}$ and ^{1}H NMR spectra at different temperatures. No reaction occurred until the temperature was raised to about 0 °C. At this temperature **1** slowly converts to the oxacyclocarbene derivatives **2** or **4**, respectively, without any evidence for the formation of intermediate species.

[$ReCl_2$(η^1-*N*-NNC(O)Ph){η^1-*N*-$NH_2CH_2C{\equiv}CH$}(PPh_3)$_2$] (6). To a suspension of **1** (200 mg, 0.22 mmol) in THF (30 mL), one equivalent of propargylamine, HC≡C(CH_2)NH_2 (15.2 μL) was

added *via* micro-syringe. The resulting deep orange solution was stirred and heated under reflux for 5 h. Concentration of the solution under nitrogen to *ca.* 10 mL and addition of diethyl ether (20 mL) gave a mixture of **6** and **7** (9 : 1) as a brownish green powder. The yield, based on rhenium, was 70%. Recrystallisation of the crude product from CH_2Cl_2–EtOH (1 : 2 v/v, 10 mL) gave a small crop of analytically pure brownish-green crystals of **6** suitable for X-ray analysis. Yield 30%, based on **1** (Found: C, 57.52; H, 4.40; N, 4.29. $C_{46}H_{40}Cl_2N_3OP_2Re$ requires C, 56.98; H, 4.16; N, 4.33%); ν_{max}/cm^{-1} 3404 (NH_2), 1654 $(CO)_{benzoyl}$, 1434 $(N{=}N)_{hydraz}$, 1305, 1252 (COPh); δ_H ($CDCl_3$), 2.14 (2H, m, $-NH_2CH_2C{\equiv}CH$), 3.75 (1H, m, $-NH_2CH_2C{\equiv}CH$), 4.15 (2H, m, $-NH_2CH_2C{\equiv}CH$), 7.2–7.9 (35H, m, Ph); δ_P ($CDCl_3$) 1.24 (d, J_{PP} 20.3 Hz), 10.10 (d, J_{PP} 20.3 Hz).

$[ReCl_2(\eta^1\text{-}N\text{-}NNC(O)Ph)\{\eta^1\text{-}N\text{-}NH_2CH_2C{\equiv}CH\}_2(PPh_3)_2]$ (7). Addition of tenfold excess of $HC{\equiv}C(CH_2)NH_2$ (2.16 mmol) following the procedure described above and similar work-up, gave a mixture of **7** and **6** (9 : 1) as a brownish-green powder. Total yield based on rhenium, 62%. An analytically pure sample of **7** was obtained upon recrystallization from CH_2Cl_2–EtOH (1 : 2 v/v, 10 mL) as described above (yield 28% based on **1**) (Found: C, 49.18; H, 4.12; N, 7.24. $C_{31}H_{30}Cl_2N_4OPRe$ requires C, 48.83; H, 3.96; N, 7.34%); ν_{max}/cm^{-1} 3300 (NH_2), 3260 (NH_2), 1658 $(CO)_{benzoyl}$, 1618 $(CO)_{benzoyl}$, 1433 $(N{=}N)_{hydrazido}$, 1305, 1252 (COPh); δ_H ($CDCl_3$), 3.80 (1H, m, $-NH_2CH_2C{\equiv}CH$), 4.17 (4H, br t, J_{HH} 7.5, $-NH_2CH_2C{\equiv}CH$), 7.15 (4H, m, $-NH_2CH_2C{\equiv}CH$), 7.2–7.8 (20H, m, Ph); δ_P ($CDCl_3$) 7.04 (s); δ_C ($CDCl_3$), 187.18 (s, $-N_2C(O)Ph$), 98.92 (s, $-NH_2CH_2C{\equiv}CH)_{trans\ to\ Cl}$ 85.20 (s, $-NH_2CH_2C{\equiv}CH)_{trans\ to\ PPh_3}$, 73.92 (s, $-NH_2CH_2C{\equiv}CH)_{trans\ to\ Cl}$, 61.95 (s, $-NH_2CH_2C{\equiv}CH)_{trans\ to\ PPh_3}$, 40.14 (s, $-NH_2CH_2C{\equiv}CH)_{trans\ to\ Cl}$, 29.90 (s, $-NH_2CH_2C{\equiv}CH)_{trans\ to\ PPh_3}$, 6.4–7.6 (30H, m, Ph).

$[ReCl_2(\eta^1\text{-}N\text{-}NNC(O)Ph)\{\eta^1\text{-}N\text{-}NH_2CH_2CH{=}CH_2\}_2(PPh_3)_2]$ (8). Addition of a stoichiometric amount of $H_2C{=}CHCH_2NH_2$ (17 μL) to a suspension of **1** (200 mg, 0.22 mmol) in THF (30 mL) and work-up as described above for **6**, yielded a brown powdered material in 66% yield. $^{31}P\{^1H\}$ NMR analysis of the crude product indicates **8** (*ca*. 82%) as the major component of a very complicated mixture of unidentified products. Recrystallization from CH_2Cl_2–EtOH (1 : 2 v/v, 10 mL) gave dark brown microcrystals of analytically pure **8** in *ca.* 40% with respect to **1**. Repeating the reaction with a tenfold proportion of allylamine does not significantly change the product distribution, but slightly increases the yield of **8** to *ca.* 90% (Found: C, 49.01; H, 4.72; N, 7.11. $C_{31}H_{34}Cl_2N_4OPRe$ requires C, 48.57; H, 4.47; N, 7.30%); ν_{max}/cm^{-1} 3298–3245 (NH_2) 1603 $(CO)_{benzoyl}$, 1447 $(N{=}N)_{hydrazido}$, 1309, 1224 (COPh); δ_H ($CDCl_3$), 3.30 (4H, m, $-NH_2CH_2CH{=}CH_2$), 3.65 (1H, br t, $^2J_{HH}$ 8.8, $-NH_2CH_2CH{=}CH_2$), 3.86 (1H, br t, $^2J_{HH}$ 10.9, $-NH_2CH_2CH{=}CH_2$), 4.52 (1H, br t, $^2J_{HH}$10.9, $-NH_2CH_2CH{=}CH_2$) 5.06 (1H, d, $^3J_{HH\,trans}$ 17.4, $-NH_2CH_2CH{=}CCH_2$), 5.17 (1H, d, $^3J_{HH\,cis}$ 10.8, $-NH_2CH_2CH{=}CCH_2$), 5.25 (1H, d, $^3J_{HH\,cis}$ 10.8, $-NH_2CH_2CH{=}CCH_2$), 5.31 (1H, d, $^3J_{HH\,trans}$17.1, $-NH_2CH_2CH{=}CCH_2$), 5.79 (1H, ddt, $^3J_{HH\,trans}$ 17.4, $^3J_{HH\,cis}$ 10.8, $^3J_{HH}$ 5.7, $-NH_2CH_2CH{=}CH_2$), 6.00 (1H, ddt, $^3J_{HH\,trans}$ 17.1, $^3J_{HH\,cis}$ 10.8, $^3J_{HH}$ 5.7, $-NH_2CH_2CH{=}CH_2$), 6.20 (1H, br t, $^2J_{HH}$ 8.8, $-NH_2CH_2CH{=}CH_2$), 7.2–7.8 (20H, m, Ph); δ_P ($CDCl_3$) 4.9 (s).

Crystal structure determinations

The crystal data for the five compounds **2**, **3a**, **3b**, **4** and **6** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation and corrected for Lorentz, polarization and absorption effects. The structures were solved by direct and Fourier methods using full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. In compound **3a** the C9(H)–C12(H_2) moiety of the 2-oxa-3-methylcyclopentylidene ring was found disordered. This fragment was refined with two independent orientations with multiplicity of 0.6 and 0.4, respectively. In compound **4** the C10(H2) and C11(H2) atoms of the 2-oxacyclohexylidene six-membered ring were found disordered and refined isotropically with two independent orientations with multiplicity of 0.6 and 0.4, respectively. The crystal data and refinement parameters are summarized in Table 2. Selected interatomic distances and angles are given in Tables 3 and 4. The program used and sources of scattering factors are given in ref. 42.

ORTEP[43] views of the five complexes are shown in Figs. 4–7. The crystals **2**, **4** and **6** contain a solvent molecule of CH_2Cl_2 per octahedral complex, while **3b** contain a solvent molecule of ethanol. The crystals **3a** and **3b** were found within the same crystallization bulk. They are polymorphic crystals differing mainly in their color, orange for **3a** and yellow for **3b**, and by the presence of a solvent molecule of ethanol in **3b**.

CCDC reference numbers 225817–225821.

See http://www.rsc.org/suppdata/dt/b3/b315693a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We are grateful to Dr S. Roma for technical assistance, Mr M. Fratta (University of Ferrara) for elemental analyses and Mr F. Cecconi (ICCOM CNR, Firenze) for magnetic measurements in the solid state. Thanks are given to MURST (Rome) and NATO (project PST.CLG.978521) for supporting this research activity and to the EC (IHP Program) for an access grant to the "Plataforma Solar de Almería" (Almería, Spain).

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