REACTIONS OF BIS(PHENYLDIAZENIDO)RHENIUM COMPLEX $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ WITH CARBON MONOXIDE AND ALK-1-YNES

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday.

The conversion of the bis(diazenido) complex $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (**1**) to the mono(diazenido) complex $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**) is promoted by alk-1-ynes, whereas the reaction with CO leads to the mixed dicarbonylmono(diazenido) Re(III) species $[ReBr(CO)_2(NNPh)(PPh_3)_2]Br$ (**3**). Both reactions are suggested to occur via related pathways involving a nucleophilic displacement of one of the diazenide ligands by Br^-. Reduction of the phenyldiazenide ligand in **2** occurs in the attempted reaction with HC≡CPh to give the nitrido complex $[ReBr_2(N)(PPh_3)_2]$ (**4**) and the bis(diazenido) species $[ReBr_2(NNPh)_2(PPh_3)_2]$ (**5**) and $[ReBr(NNPh)_2(PPh_3)_2]$ (**6**).

Keywords: Alkynes; Carbonyl complexes; Rhenium; Diazenido complexes; Diazenes; N ligands; Coordination chemistry.

Considerable attention has been paid to the coordination chemistry of organodiazenides[1–5], versatile ligands that are known to display either single- or double-bent geometries with distinct electron-donor abilities, and that are of importance in major fields such as nitrogen fixation[6–11], radiopharmaceutical development[1,12–17] and catalysis[18–20].

In previous studies and in pursuit of our interest on the activation of unsaturated small molecules with transition metal centers[21–27], we have investigated the reactions of organodiazenido complexes with isocyanides (C≡NR)[28–30], cyanamides ($N{\equiv}C{-}NR_2$)[31] and phosphirene $\overline{\mathrm{PPhCPh{=}C}}\mathrm{Ph}$[32]. The organodiazenide ligand can either remain coordinated to the metal or undergo decomposition to N_2 and an organic derivative. Examples include the formation of (i) the mixed diazenido-isocyanido complexes $[ReBr_2$-

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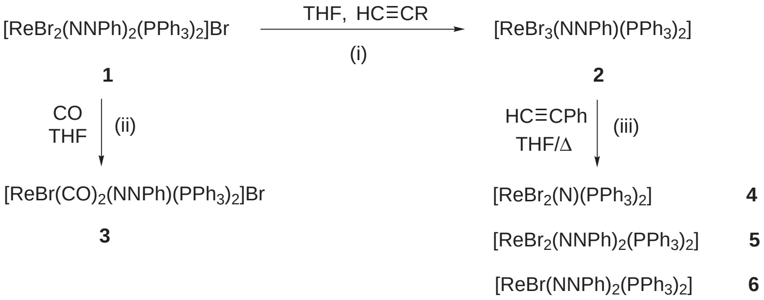
$(CNR)(NNPh)(PPh_3)_2]$ (R = Me, 4-ClC_6H_4), $[ReBr_2(CNMe)_2(NNPh)(PPh_3)]$ or $[ReBr(CNMe)_2(NNPh)(PPh_3)_2]$ from reactions of isocyanides with $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (**1**), $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**) or $[ReBr_2(NNPh)_2(PPh_3)_2]$ [28,33]; (ii) the mixed dinitrogen-isocyanido complexes $[ReCl(CNR)(N_2)\{P(OR)_3\}_{3-x}(PPh_3)_x]$ (x = 0, 1) from reactions of isocyanides with $[ReCl_2(NNCOPh)\{P(OR)_3\}_{3-x}(PPh_3)_x]$ (x = 0, 1) in the presence of MeOH [30]; (iii) the organocyanamido complexes *mer*-$[ReCl(N_2)(NCNR_2)L_3]$ (L = $PMePh_2$; R = Me, Et) and *mer*-$[ReCl_2(NCNEt_2)L_3]$ from reactions of the organocyanamides with $[ReCl_2(NNCOPh)L_3]$, in the presence of MeOH [31]; (iv) the mixed phenyldiazenido-phosphirene complex $[ReBr(NNPh)_2(\overline{PPhCPh{=}C}Ph)_2(PPh_3)]$ from the reaction of triphenylphosphirene with $[ReBr_3(NNPh)(PPh_3)_2]$ [32]. In reactions (ii) and (iii), the phenyldiazenide ligand decomposed to dinitrogen and methyl benzoate ($PhCO_2Me$) upon nucleophilic attack by methoxide.

In the current study, we have extended the reactions of some of the above diazenido complexes, i.e. the bis(diazenido) complex $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (**1**) and the mono(diazenido) complex $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**), to other unsaturated substrates, viz. carbon monoxide and alk-1-ynes. We have found that the latter compounds promote the conversion of **1** into **2**, while the reaction of **1** with CO leads to the mixed diazenido-dicarbonyl complex $[ReBr(CO)_2(NNPh)(PPh_3)_2]Br$ (**3**). Both reactions seem to occur in closely related pathways. In addition, the phenyldiazenide ligand in **2** undergoes complete reductive N=N bond cleavage, converting it to nitride, in $[ReBr_2(N)(PPh_3)_2]$ (**4**), upon attempted reaction of **2** with HC≡CPh in refluxing tetrahydrofuran, also with the formation of the bis(diazenido) complexes $[ReBr_2(NNPh)_2(PPh_3)_2]$ (**5**) and $[ReBr(NNPh)_2(PPh_3)_2]$ (**6**).

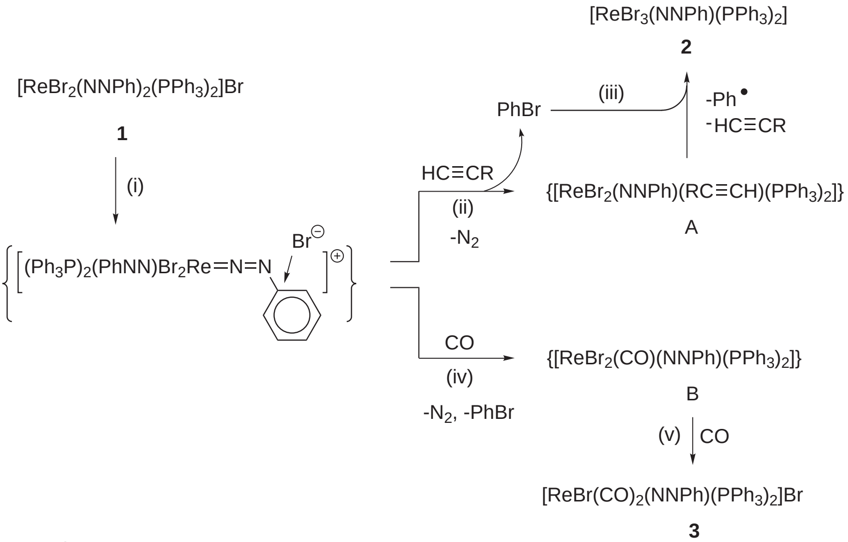
RESULTS AN DISCUSSION

The bis(phenyldiazenido) complex $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (**1**) is known[28] to convert spontaneously (in THF or acetone solutions) into the mono(phenyldiazenido) complex $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**). However, this reaction is rather slow and typically requires 3–4 days (in THF) in order to get a good yield. We have now observed that the reaction can be promoted by alk-1-ynes HC≡CR, such as HC≡CPh or HC≡CCOOMe, giving a good conversion already after 24 h, in THF at ambient temperature (Scheme 1, reaction (i)).

The promoting effect of the alkyne conceivably results from favoring the formation of a dibromido-mono(diazenido) intermediate, as suggested in Scheme 2. Nucleophilic attack of the Br^- counterion to the *ipso*-carbon of NNPh to form PhBr is a possible reaction (Scheme 2, reactions (i) and (ii)) on account of the high IR ν(NN) frequencies in **1** (1845, 1755, 1575 and 1565 cm^{-1}, in KBr pellet), reflecting the expected weak π-electron acceptance of the diazenide ligand from the high-oxidation-state metal, Re(V)[28,34]. The abstraction of the phenyl group from coordinated NNPh leaves a labile dinitrogen ligand that can be replaced by alk-1-yne to form the postulated mono(diazenido) intermediate $[ReBr_2(NNPh)(PPh_3)_2(RC{\equiv}CH)]$ (**A**) which could form the final product $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**) on reaction with the liberated PhBr, via C–Br bond homolysis and loss of the RC≡CH ligand (Scheme 2, reaction (iii)). It is noteworthy to mention that



SCHEME 1



SCHEME 2

the acetonitrile complex [$ReBr_2(MeCN)(NNPh)(PPh_3)_2$] analogous to **A** can be prepared and, in fact, reacts with PhBr to yield **2**[35], thereby supporting our hypothesis.

The proposed mechanism is also consistent with the formation of the mixed dicarbonylmono(diazenido) complex [$ReBr(CO)_2(NNPh)(PPh_3)_2$]Br (**3**) by the reaction of [$ReBr_2(NNPh)_2(PPh_3)_2$]Br (**1**) with CO (Scheme 1, reaction (ii)) in THF at ambient temperature (CO was added by bubbling it through a suspension of **1** in THF). In fact, the postulated carbonylmono(diazenido) intermediate [$ReBr_2(CO)(NNPh)(PPh_3)_2$] (**B**), analogous to the alk-1-yne species **A**, would be formed by a pathway (Scheme 2, reactions (i) and (iv)) identical to that discussed above. However, the expected higher inertness of the CO ligand to displacement in **B** in comparison with the higher lability of the alk-1-yne in **A**, prevents complex **B** from following a further reaction identical to that of **A** (Scheme 2, reaction (iii)) to give [$ReBr_3(NNPh)(PPh_3)_2$] (**2**), which would require the loss of the CO ligand. Instead, **A** reacts further with CO (present in an excess) to give, via Br^- ligand replacement, the final dicarbonyl complex [$ReBr(CO)_2(NNPh)(PPh_3)_2$]Br (**3**) (Scheme 2, reaction (v)).

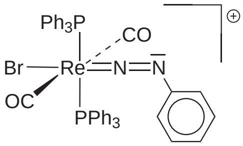
Moreover, species **B** is analogous to the reported[28] isocyanido complex [$ReBr_2(MeNC)(NNPh)(PPh_3)_2$] that, in the presence of an excess of MeCN in THF affords the bis(isocyanido) products [$ReBr_2(MeCN)_2(NNPh)(PPh_3)$] and [$ReBr(MeNC)_2(NNPh)(PPh_3)_2$].

Complex **3**, isolated as an orange microcrystalline solid (45% yield), was characterized by IR, ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopies, and elemental analysis. In the IR spectrum of **3**, ν(CO) is observed as a strong band at 2000 cm^{-1} which compares well with those quoted for other diazenido-dicarbonyl complexes, such as the Re(III) compound [$ReCl_2(CO)_2(NNCOPh)$-$(PPh_3)_2$] (2005 and 1910 cm^{-1})[36] and [$RuBr(CO)_2(NNPh)(PPh_3)_2$] (2043 and 1984 cm^{-1})[37].

However, in our case, the observation of the single ν(CO) band indicates that the CO ligands are in a mutually trans position. The ν(NN) absorption of the diazenide ligand in **3** is found at 1660 and 1570 cm^{-1}. The wavenumbers are smaller than those exhibited by **1** (1845, 1755, 1575 and 1565 cm^{-1}) and **2** (1700 and 1575 cm^{-1}), in agreement with the lower oxidation state of Re(III) in **3**, with resulting higher π-electron release from the metal. The appearance of more than one ν(NN) band per each aryldiazenide ligand is common, due to coupling with vibrational modes of the aryl group[38].

The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet at δ –151.5 relative to $P(OMe)_3$, which suggests the trans arrangement of the two phosphanes. Hence, the molecular structure of complex **3** is expected to adopt form **a**

(Chart 1), with mutually trans CO and PPh_3 ligand pairs, and the diazenide ligand with the single-bent geometry (three-electron donor) importing a formal 18-electron count to the complex.



a

CHART 1

Although $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**) does not appear to react with alk-1-ynes at ambient temperature in THF, heating to reflux for 2 days in the presence of HC≡CPh (six-fold molar excess) leads to the formation of the nitrido complex $[ReBr_2(N)(PPh_3)_2]$ (**4**), together with the bis(diazenido) products $[ReBr_2(NNPh)_2(PPh_3)_2]$ (**5**) and $[ReBr(NNPh)_2(PPh_3)_2]$ (**6**), isolated in low yields (ca. 15% each) as brick-red (**4**), red (**5**) and orange (**6**) microcrystalline solids.

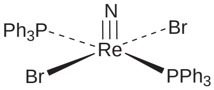
The formation of the nitrido complex **4** involves complete cleavage of the N=N bond of the diazenide group NNPh in **2**. The pathway is unknown, but it may involve protonation of the diazenido- to hydrazido-type {Re=N–NHPh} species, which, upon further reduction, would lead to the nitrido {Re≡N} product and aniline ($PhNH_2$), with alk-1-yne acting as the proton or hydrogen source. Rhenium(IV) in **2** behaves as a reducing agent, being oxidized to Re(V) in **4**.

The reduction of an organohydrazide (NNR_2) ligand to nitride has been reported in a few cases but with the requirement for a reducing agent other than the metal, to which the hydrazide is coordinated. Hence, the nitride complexes $[Mo(N)(ArN_3N)]$ (ArN_3N^{3-} = triamidoamine = $[(ArNCH_2CH_2)_3N]^{3-}$; Ar = 4-FC_6H_4, 4-$Bu^tC_6H_4$, C_6F_5)[39] and $[Mo(N)(O\text{-}1\text{-}Ad)_3]$ (1-Ad = 1-adamantyl)[40] are formed upon reduction of the corresponding dimethylhydrazine ($NNMe_2$) complexes with sodium amalgam and cobaltocene, respectively. These reactions are not yet fully understood and the nitrido products are formed in low yields.

It is also noteworthy to mention that complex **4** and its dichlorido analogue $[ReCl_2(N)(PPh_3)_2]$ were previously prepared by using the appropriate hydrazinium salt $N_2H_4{\cdot}2HX$ (X = Br and Cl, respectively) as the source of the nitride ligand[41,42]. The starting rhenium material can be a perrhenate salt, rhenium heptoxide or $[ReCl_3(O)(PPh_3)_2]$. The reaction proceeds in boiling ethanol or methanol, in the presence of an excess of PPh_3 (oxygenatom abstractor)[41,42]. The procedures usually require a careful control of experimental conditions, e.g., moist (rather than dried) ethanol is necessary[41] in the case of [$ReCl_3(O)(PPh_3)_2$]. In these reactions, ammonium is the other expected product resulting from the degradation of hydrazinium[41].

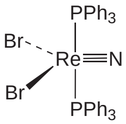
In our case, the formation of the bis(diazenido) products [$ReBr_2(NNPh)_2$-$(PPh_3)_2$] (**5**) and [$ReBr(NNPh)_2(PPh_3)_2$] (**6**) from mono(diazenido) complex [$ReBr_3(NNPh)(PPh_3)_2$] (**2**) is also intriguing and proceeds conceivably via dinuclear species with bridging bromide, diazenide or derived ligands, allowing their transfer from one metal to another one. Comparable conversions were observed[32] in the reaction of **2** with triphenylphosphirene, in refluxing THF, yielding also complex **5** and the Re(III) phosphirene complex [$ReBr(NNPh)_2(PPh_3)(PPhCPh{=}CPh)_2$] (ca. 20% yield), which relates to **6**.

The nitrido complex [$ReBr_2(N)(PPh_3)_2$] (**4**) was characterized by IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopies and elemental analysis. The strong IR band at 1090 cm^{-1} is assigned to ν(ReN) and the observed $^{31}P\{^1H\}$ NMR singlet at δ –117.90, relative to $P(OMe)_3$, points to equivalence of the two phosphane ligands. The color and the IR spectrum of **4** are identical to those of the analogous dichlorido complex [$ReCl_2(N)(PPh_3)_2$] (whose lack of solubility in common solvents precluded recording its NMR spectra). Therefore, it is expected that **4** exhibits a molecular structure similar to that of the latter complex, which has been established by single-crystal X-ray diffraction[43]. Hence, it can be predicted as either a distorted tetragonal pyramid (Chart 2, **b**) with the nitride at the apex and the bulky phosphanes mutually trans in the basal plane, or a distorted trigonal bipyramid (Chart 3, **c**) with the phosphanes at the apical positions.



b

CHART 2



c

CHART 3

Complexes **5** and **6** were identified by elemental analyses and similarity of their spectroscopic features to those reported[28,44–46] previously for such compounds.

The bis(diazenido) complex [$ReBr_2(NNPh)_2(PPh_3)_2$]Br (**1**) has been shown to be a promising entry to the syntheses of mono(diazenido) derivatives, its conversion to [$ReBr_3(NNPh)(PPh_3)_2$] (**2**) being promoted by the presence of a labile alk-1-yne. However, if a substrate such as CO, which can bind as a stronger ligand, is used, a mono(diazenido) product with such a ligand is obtained. In this way, a dicarbonylmono(diazenido) compound was prepared and, thus, the work extends a previous study[28] undertaken with isocyanides.

These reactions suggest a nucleophilic displacement of the phenyl group from one of the phenyldiazenide ligands in **1**, proposed to occur via nucleophilic attack of the Br^- counterion to the *ipso*-carbon of such a phenyl moiety.

The phenyldiazenide ligand undergoes an unusual reduction with the Re(IV) binding center in **2** to yield a nitride (N^{3-}), upon complete N=N bond cleavage, in the presence of an acid alk-1-yne. A dibromido-nitrido complex is thus formed, although the selectivity is still modest due to the competition of the transfer of the ligated diazenide to another metal, yielding bis(diazenido) products.

The synthetic applications of all these uncommon reactions deserve to be further explored.

EXPERIMENTAL

Solvents used were dried and degassed by using standard techniques. All reactions were performed under an inert atmosphere of dry nitrogen. Phenylhydrazine, CO, alk-1-ynes and HBr were commercially available and used without further purification. Complex **1** was prepared according to a published procedure[28]. IR spectra (ν, cm^{-1}) were run with a Perkin–Elmer 683 spectrometer, NMR spectra on a Varian Unity 300 spectrometer; δ values are in ppm relative to $SiMe_4$ (^1H) or $P(OMe)_3$ (^{31}P).

$[ReBr_3(NNPh)(PPh_3)_2]$ (**2**)

HC≡CR (85 μl (R = Ph) or 69 μl (R = COOMe), 0.78 mmol) was added to a suspension of $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (0.15 g, 0.13 mmol) in THF (50 ml) and the system was stirred for 24 h. Concentration of the dark green solution in vacuo to ca. 10 ml, followed by addition of pentane, resulted in the precipitation of **2** as a green solid that was filtered off, washed with pentane and dried in vacuo. Further crops of **2** were obtained from the mother liquor upon concentration and addition of pentane (yield ca. 50–55%). IR (KBr pellet): 1700 ms, 1575 s (ν(NN)). The IR spectrum and elemental analysis were consistent with the formulation and with data reported earlier[28].

$[ReBr(CO)_2(NNPh)(PPh_3)_2]Br$ (**3**)

Carbon monoxide was bubbled for a few minutes via a glass frit through a stirred suspension of $[ReBr_2(NNPh)_2(PPh_3)_2]Br$ (**1**) (0.15 g, 0.13 mmol) in THF (40 ml). The resulting dark green solution was stirred for 24 h to gradually turn orange. Concentration in vacuo to ca. 10 ml and addition of pentane caused precipitation of **3** as an orange solid that was filtered off and dried in vacuo. Another crop of **3** was obtained on further concentration of the mother liquor and addition of pentane. Recrystallization from CH_2Cl_2/Et_2O resulted in an orange microcrystalline precipitate of **3** that was filtered off, washed with Et_2O and dried in vacuo (yield 45%). For $C_{44}H_{35}Br_2N_2O_2P_2Re \cdot 2(C_2H_5)_2O$ (1179.9) calculated: 52.9% C, 4.7% H, 2.4% N; found: 53.3% C, 4.6% H, 2.9% N. IR (KBr pellet): 2000 s (ν(CO)); 1660 s, 1570 s (ν(NN)). ^1H NMR ($CDCl_3$): 7.92–7.18 m, 30 H ($P(C_6H_5)_3$); 7.15–6.46 m, 5 H (NNC_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): –151.49 s.

$[ReBr_2(N)(PPh_3)_2]$ (**4**)

HC≡CPh (111 μl, 1.0 mmol) was added to a suspension of $[ReBr_3(NNPh)(PPh_3)_2]$ (**2**) (0.18 g, 0.17 mmol) in THF (60 ml). The system was heated to reflux for 48 h, yielding gradually a red solution. The latter was concentrated to ca. 10 ml and pentane was added, whereupon the system was left for 1 day. The precipitate formed was separated by filtration and recrystallized from CH_2Cl_2/Et_2O to give a brick-red microcrystalline **4** that was filtered off, washed with Et_2O and dried in vacuo (yield 15%). The mother liquor was taken to dryness to give an oily residue. Addition of Et_2O followed by vigorous stirring resulted in a dark-red solid. Its recrystallization from CH_2Cl_2/Et_2O afforded, as a first crop, an orange precipitate of $[ReBr(NNPh)_2(PPh_3)_2]$ (**6**) (yield 15%) and, in a second crop, a red precipitate of $[ReBr_2(NNPh)_2(PPh_3)_2]$ (**5**) (yield 10%).

Complex **4**: For $C_{36}H_{30}Br_2NP_2Re \cdot 2(C_2H_5)_2O$ (1032.8) calculated: 51.1% C, 4.9% H, 1.4% N; found: 51.2% C, 4.3% H, 1.8% N. IR (KBr pellet): 1090 vs (ν(ReN)). ^1H NMR ($CDCl_3$): 7.83–7.44 m ($P(C_6H_5)_3$). $^{31}P\{^1H\}$ NMR: –117.90 s.

Complex **5**: For $C_{48}H_{40}Br_2P_2Re$ (1024.8) calculated: 53.3% C, 3.7% H, 5.2% N; found: 53.7% C, 3.6% H, 5.0% N. IR (KBr pellet): 1625 m, 1585 w, 1560 s (ν(NN)).

Complex **6**: For $C_{48}H_{40}BrP_2Re$ (944.9) calculated: 57.6% C, 4.0% H, 5.6% N; found: 57.7% C, 4.1% H, 5.7% N. IR (KBr pellet): 1540 s, 1510 s (ν(NN)).

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