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Synthesis, structure, and reactivity of rhenium *N*-isocyanide complexes $ReBr(CO)_3(CNR)(CNNPPh_3)$

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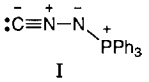
Abstract

The rhenium isocyanide complex $ReBr(CO)_3(CNR)(NCMe)$ (**1**) reacted with $CNNPPh_3$ in CH_2Cl_2 to give $ReBr(CO)_3(CNR)(CNNPPh_3)$ (**2a**, R = Ph; **2b**, R = Pr) in good yields. Treatment of **2** with ketones in the presence of a catalytic amount of HBF_4 yielded the derivatives $ReBr(CO)_3(CNR)(CNN{=}CR'R'')$ (**3**). The complex $ReBr(CO)_3(CNR)(CNN{=}CMe_2)$ on reaction with isopropylamine gave the amino(hydrazono)carbene complex $ReBr(CO)_3(CNR)\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**4**). Prolonging the reaction of **3a** (R = Ph, R′ = R″ = Me) with isopropylamine in $CDCl_3$, it was converted first into $ReBr(CO)_3(CNPh)\{C(NHPr^i)(NHN{=}CMe_2)\}$, followed by the formation of the biscarbene product $ReBr(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**5**). The complexes $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**) and $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) have been characterized by single-crystal X-ray diffraction analyses.

Keywords: Rhenium; Isocyanide; Carbene; Amine; Structure

1. Introduction

The *N*-isocyanoiminetriphenylphosphorane ($CNNPPh_3$) is a unique *N*-isocyanide reagent, which can be described by the interesting resonance formula **I** [1].



I

Although this *N*-isocyanide ligand is versatile and has been known for many years, its chemistry has been surprisingly less explored [1,2]. In the course of our interest in studying the chemistry of isocyanide complexes, we have previously reported the preparation of diaminocarbene complexes $ReBr(CO)_4\{C(NHPh)(NHR)\}$, and their successive, reversible orthometalation reactions [3]. Recently, we have also presented the activation of $ReBr(CO)_4(CNR)$ to form the labile intermediates $ReBr(CO)_3(CNR)(NMe_3)$ and $ReBr(CO)_3(CNR)(NCMe)$ with the aim of preparing related derivatives and gaining more insights into the chemistry of the rhenium isocyanide complexes [4]. Considering the capability of the $CNNPPh_3$ ligand to undergo Wittig-type reactions [1,2], and the important applications of carbene complexes [5,6], we therefore explored the subtle reactivity differences between coordinated CNR and CNNR toward nucleophiles to form carbene derivatives on the same metal center or metal clusters. In this paper, we report the synthesis of isocyanide

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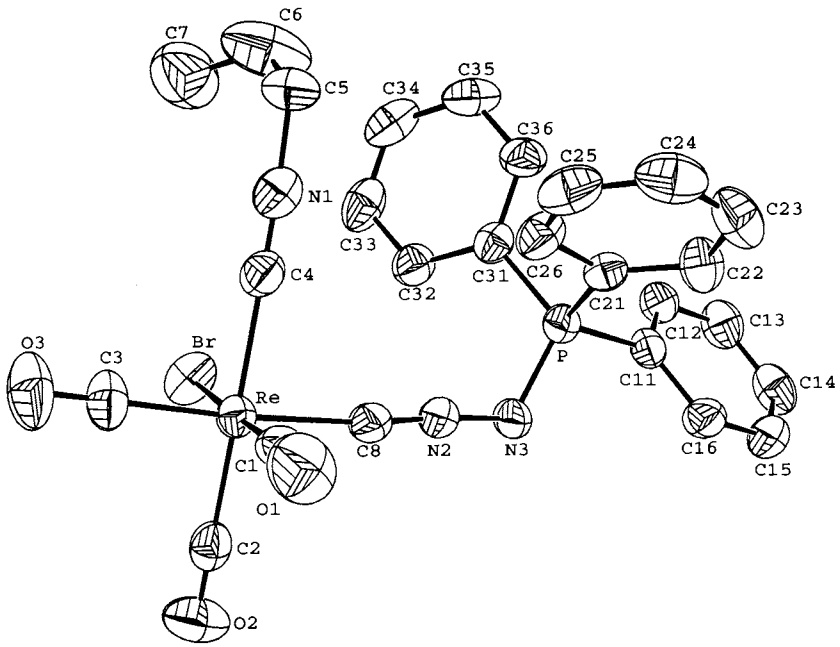


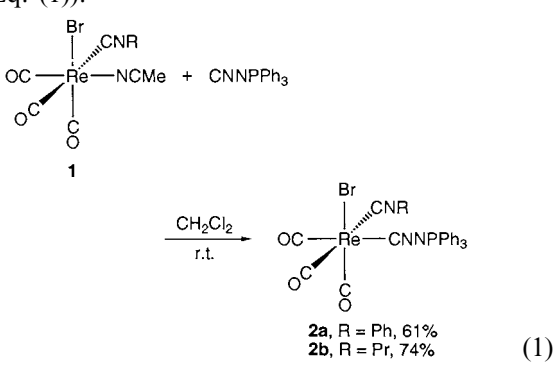
Fig. 1. ORTEP diagram of $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**).

derivatives $ReBr(CO)_3(CNR)(CNNPPh_3)$ and their reactivities. The coordinated CNNR is found to be more reactive toward amines than the CNR ligand. A comparison is also made to account for the reactivity difference between these coordinated isocyanide and *N*-isocyanoimine ligands, CNR and CNNR.

2. Results and discussion

2.1. Preparation of complex $ReBr(CO)_3(CNR)(CNNPPh_3)$ (2)

Treatment of the 'lightly-stabilized' complex $ReBr(CO)_3(CNR)(NCMe)$ (**1a**, R = Ph; **1b**, R = Pr) with $CNNPPh_3$ readily afforded $ReBr(CO)_3(CNR)(CNNPPh_3)$ (**2a**, R = Ph; **2b**, R = Pr) in moderate to high yield (Eq. (1)).



(1)

Complexes **2a** and **2b** were slightly unstable in solution and were isolated as white microcrystalline solids. The IR spectrum of **2b** showed that the $\nu(C{\equiv}N)$ absorptions of the terminally co-ordinated isocyanide (CNPr) and

Table 1
Crystal and intensity collection data for $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**) and $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**)

	2b	**3a**
Empirical formula	$C_{26}H_{22}BrN_3O_3PRe$	$C_{14}H_{11}BrN_3O_3Re$
Formula weight	721.56	535.37
Space group	*Pbca*	$P2_1/n$
Unit cell dimensions		
a (Å)	9.209 (1)	6.268 (1)
b (Å)	19.079 (2)	14.663 (3)
c (Å)	30.035 (3)	19.145 (6)
β (°)		96.84 (2)
V (Å^3)	5277.1 (10)	1746.9 (8)
$D_{calc.}$ (g cm^{-3})	1.816	2.036
Z	8	4
Crystal dimension (mm)	$0.31 \times 0.25 \times 0.19$	0.25×0.31
		$\times 0.44$
Absorption coefficient μ(Mo–K$_\alpha$) (mm^{-1})	6.26	9.3293
Temperature	Room temperature	Room temperature
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
2Θ (max)	46.7	50.0
Scan type	$\omega/2\theta$	$\omega/2\theta$
Total no. of reflections	3867	3373
No. of observed reflections $F_o > 2.5\sigma(F_o)$	2587	2174
Observed variables	316	200
R	0.028	0.029
$wR(F^2)$	0.033	0.035
Δ (ρ) (e Å^{-3})	0.810	−0.780
Δ/σ_{max}	0.089	0.0005
G-O-F	1.53	1.62

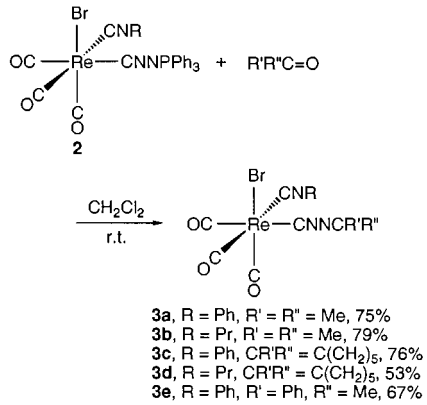
Table 2
Selected bond distances (Å) and angles (°) for $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**)

Bond distances			
Re–C(1)	1.960(9)	Re–Br	2.6313(9)
Re–C(2)	1.958(9)	P–N(3)	1.624(6)
Re–C(3)	1.940(8)	N(1)–C(4)	1.16(1)
Re–C(4)	2.067(8)	N(2)–N(3)	1.343(8)
Re–C(8)	2.119(8)	N(2)–C(8)	1.14(1)
Bond angles			
Br–Re–C(8)	84.8(2)	C(3)–Re–C(8)	175.5(3)
C(4)–N(1)–C(5)	176.4(8)	C(4)–Re–C(8)	85.2(3)
N(3)–N(2)–C(8)	173.9(7)	P–N(3)–N(2)	113.9(4)
Re–C(4)–N(1)	177.7(7)	Re–C(8)–N(2)	173.2(6)

N-isocyanide ($CNNPPh_3$) were overlapped at 2207 cm^{-1}. The ^{31}P-NMR spectrum of **2b** showed a singlet at δ 32.14 attributed to the P atom of the $CNNPPh_3$ group. This resonance is close to those of $M(CO)_5(CNNPPh_3)$ (M = Cr, Mo, W) implying that the $CNNPPh_3$ ligand is terminally coordinated [1]. In addition to spectroscopic determination, the structure of **2b** was also characterised by single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecule is shown in Fig. 1; relevant crystallographic details are listed in Tables 1 and 2. The molecule contains a rhenium atom in a distorted octahedral environment with three CO groups arranged in a facial configuration. The CNN atoms of the terminally coordinated $CNNPPh_3$ ligand are almost linear with a C(8)–N(2)–N(3) bond angle of 173.9(7)°. A partial double-bond character exists between N(2)–N(3) with a distance of 1.343(8) Å, whereas the C(8)–N(2) bond length is 1.14(1) Å indicating a triple-bond character [7]. The isocyanide ligand remains near linear with a C(4)–N(1)–C(5) bond angle of 176.4(8)° and the C(4)–N(1) vector is a typical triple bond with a distance of 1.16(1) Å [7].

2.2. Reaction of $ReBr(CO)_3(CNR)(CNNPPh_3)$ (2) with ketones

Upon treatment with ketones at room temperature (r.t.) in the presence of catalytic amount of HBF_4, complex **2** was converted to the *N*-isocyanoimine complex $ReBr(CO)_3(CNR)(CNN{=}CR'R'')$ (**3a**, R = Ph, R′ = R″ = Me; **3b**, R = Pr, R′ = R″ = Me; **3c**, R = Ph, CR′R″ = $C(CH_2)_5$; **3d**, R = Pr, CR′R″ = $C(CH_2)_5$; **3e**, R = Ph, R′ = Ph, R″ = Me) (Eq. (2)).

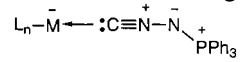


(2)

The IR spectrum of **3b** exhibited the characteristic C≡N stretching absorption at 2210 and 2154 cm^{-1} for coordinated C≡NPr and C≡NNCMe$_2$, respectively. The ^1H-NMR spectrum of **3b** showed that two methyl groups of the CNN=CMe$_2$ moiety resonated at δ 2.31 and 2.17, respectively, indicating that these two methyl groups are nonequivalent due to the restricted rotation about the C=N double bond.

Using the single-crystal X-ray diffraction method the structure of complex **3a** was obtained as shown in Fig. 2. General data and collection procedures are listed in Table 1, and selected bond distances and angles are given in Table 3. Pseudo-octahedral geometry is observed around the Re atom and the three CO ligands are arranged in a facial configuration. The *N*-isocyanoimine ligand shows a triple-bond character for C(11)–N(2) bond (1.15(1) Å), a partial double-bond character for N(2)–N(3) bond (1.38(1) Å), and a double-bond character for N(3)–C(12) bond (1.25(1) Å). The arrangement of C(11)–N(2)–N(3) is near linear (168.9(8)°), whereas N(2)–N(3)–C(12) is bent with an angle of 113.8(8)°. The isocyanide ligand remains linear similar to that found for **2b** and other rhenium isocyanide complexes [4].

Results from single-crystal X-ray diffraction analysis of **2b** revealed that the structure of the coordinated $CNNPPh_3$ could be described by the resonance form **II** similar to its uncoordinated configuration [1].



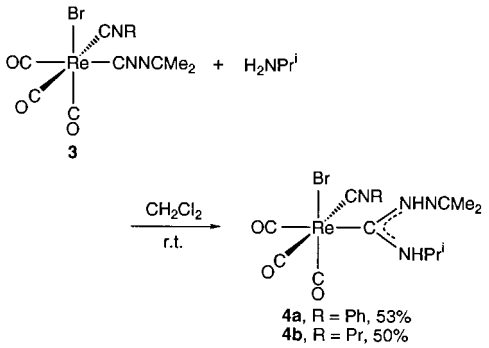
II

As a consequence, the coordinated $CNNPPh_3$ in $ReBr(CO)_3(CNR)(CNNPPh_3)$ (**2**) is capable of reacting with ketones by following the Wittig-type reaction pathway to form complex **3**, similar to that in $M(CO)_5(CNNPPh_3)$ (M = Cr, Mo, W) as reported by Fehlhammer [1,2]. The ylide-type reactions of complexes **2a** and **2b** with ketones took place very efficiently in the presence of catalytic amount of HBF_4 and were complete in a few minutes.

2.3. Reaction of $ReBr(CO)_3(CNR)(CNN{=}CMe_2)$ with isopropylamine

The complex $ReBr(CO)_3(CNR)(CNN{=}CMe_2)$ (**3a**, R = Ph; **3b**, R = Pr) on reaction with isopropylamine

readily yielded $ReBr(CO)_3(CNR)\{C(NHPr^i)(NHN{=}CMe_2)$ (**4a**, R = Ph; **4b**, R = Pr) in which the coordinated *N*-isocyanoiminoalkane ligand has undergone a nucleophilic attack by the amine to give the amino(hydrazono)carbene group. (Eq. (3)).



(3)

The ^{1}H-NMR spectrum of **4a** exhibited two broad sets of *H*N resonances at δ 9.73 and 7.97, assigned to the N*H*N=CMe_2 and N*H*Pr^i of the carbene ligand, respectively. The IR spectrum of **4** showed the same absorption pattern in the ν_{CO} stretching region (**4a**: ν(CO) 2026 (s), 1960 (s), 1901 (s) cm^{-1}) as the related complexes **2** and **3**, indicating that the three CO ligands are arranged in a facial configuration [8].

Treatment of $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) with excess isopropylamine at r.t. for 1 day afforded the biscarbene complex $ReBr(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**5**), in which both CNR and $CNN{=}Me_2$ moieties have converted to diaminocarbene and amino(hydrazono)carbene groups, respectively. The ^{1}H-NMR spectrum of **5** exhibited a broad singlet at δ 8.51 and a broad doublet at δ 6.29 assigned to the *H*N resonances of NHPh and $NHPr^i$ groups, respectively, in the diaminocarbene $C(NHPr^i)(NHPh)$ moiety. Another two broad peaks at δ 9.45 and 7.86 are attributed to the *H*N resonances of NHN=CMe_2 and $NHPr^i$, respectively, in the amino(hydrazono)carbene C(NHR)(NHN=CMe_2) group.

Table 3
Selected bond distances (Å) and angles (°) for $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**)

Bond distances (Å)			
Re–Br	2.610(1)	O(2)–C(2)	1.12(1)
Re–C(1)	2.04(1)	O(3)–C(3)	1.13(1)
Re–C(2)	1.96(1)	N(1)–C(4)	1.15(1)
Re–C(3)	1.97(1)	N(1)–C(5)	1.40(1)
Re–C(4)	2.069(9)	N(2)–N(3)	1.38(1)
Re–C(11)	2.07(1)	N(2)–C(11)	1.15(1)
O(1)–C(1)	0.90(1)	N(3)–C(12)	1.25(1)
Bond angles (°)			
Br–Re–C(1)	175.3(3)	N(3)–N(2)–C(11)	168.9(8)
C(2)–Re–C(4)	177.6(3)	N(2)–N(3)–C(12)	113.8(8)
C(3)–Re–C(11)	177.1(4)	Re–C(4)–N(1)	177.2(8)
C(4)–N(1)–C(5)	179.4(9)	Re–C(11)–N(2)	177.7(8)

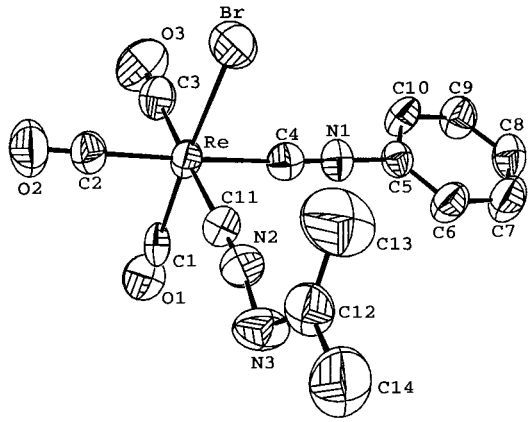
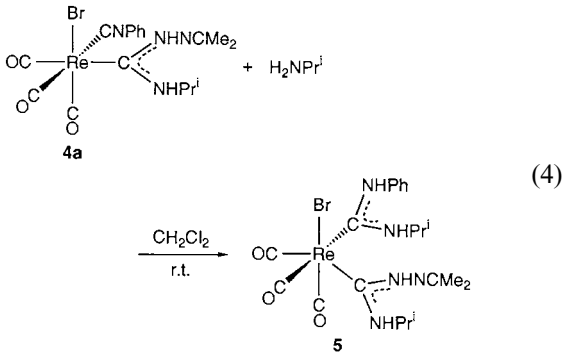


Fig. 2. ORTEP diagram of $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**).

2.4. In situ ^{1}H-NMR study on the reactivity of $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ towards isopropylamine

Continuing the reaction of $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) with excess isopropylamine in $CDCl_3$ at r.t, **3a** was initially converted to the amino(hydrazono)carbene complex $ReBr(CO)_3(CNPh)\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**4a**), which then slowly transformed to the biscarbene complex $ReBr(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**5**) as indicated by an in situ ^{1}H-NMR study. During the reaction, the ^{1}H-NMR spectra showed that a trace amount of a new species was generated after the formation of **5**. Several very small resonances at δ 7.82 (overlapped with δ 7.86), 7.13(m), and 6.98(m) might be attributed to a metallated C_6H_4 group of the by-product. Other small peaks at δ 8.36(s) and 6.14(d) might correspond to the N*H*C_6H_4 and $NHPr^i$ of the suggested carbene $C(NHPr^i)(NHC_6H_4)$ group. Thus we suggested that a trace amount of the cyclometallated complex $Re(CO)_3\{\eta^2\text{-}C(NHPr^i)(NHC_6H_4)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ might be formed during the reaction, since the ^{1}H-NMR spectrum exhibited the characteristic peaks of metallation of the phenyl group at the *ortho* position [3,9]. Unfortunately, due to the complexity of the spectrum and the difficulty of separation, this new complex has not been fully characterized.

It is believed that the carbene complex **4a** further reacted with an additional equivalent of amine to give complex **5**, in which both the coordinated *N*-isocyanoimine ($CNN{=}CMe_2$) and the isocyanide (CNPh) ligands have undergone nucleophilic attack by the amine to afford two carbene groups (Eq. (4)).



(4)

Complex **5** could not be obtained analytically pure after chromatography and recrystallisation as it was contaminated with a small amount of **4a** and other impurities. Nevertheless, its yield observed by in situ ^{1}H-NMR study was more than 70%. The FAB mass spectrum of the crude product showed the existence of **5** with the molecular ion peak at m/z 655 and subsequent CO-loss fragments. This molecular ion peak was also confirmed by comparing the isotope-distribution pattern of the theoretical value.

In comparison with **4a**, the aliphatic isocyanide group CNPr in the complex $ReBr(CO)_3$-(CNPr){C(NHPr^i)(NHN=CMe$_2$)} (**4b**) failed to react further with isopropylamine to form the biscarbene product. This is similar to the reactivity of $ReBr(CO)_4$(CNPr) and $ReBr(CO)_3(NH_2R)$(CNPr), in which the electron-releasing property of the propyl group effectively decreases the electrophilic character of the coordinated carbon of the CNPr ligand and subsequently makes it inactive toward nucleophilic attack by amines [4,10]. These results are in accord with the observations that metal complexes containing an aromatic isocyanide ligand show remarkable differences in reactivity toward nucleophilic reagents compared to their aliphatic analogues [11,12].

2.5. Reactivity difference between $ReBr(CO)_4$(CNPh) and $ReBr(CO)_3$(CNPh)(CNN=CMe$_2$) toward amines

We have previously reported that the coordinated phenyl isocyanide in $ReBr(CO)_4$(CNPh) is susceptible to nucleophilic attack by primary amines to afford the diaminocarbene complex $ReBr(CO)_4${C(NHR)(NHPh)} [10]. It is interesting to note that in the case of $ReBr(CO)_3$(CNPh)(CNN=CMe$_2$) (**3a**), the *N*-isocyano imine ligand CNN=CMe$_2$ preferentially undergoes nucleophilic attack by isopropylamine to form an amino(-hydrazono)carbene moiety {C(NHPr^i)(NHN=CMe$_2$)}. The coordinated CNPh could subsequently react with an additional equivalent of amine at r.t. to form the biscarbene complex **5**. The similar reactivity of the coordinated CNN=CMe$_2$ in $W(CO)_5$(CNN=CMe$_2$) with amines was observed by Fehlhammer [1]. Our results revealed that complex $ReBr(CO)_3$(CNPh)(CNN=CMe$_2$) (**3a**) provides a good example for comparison of the relative reactivities among the coordinated CO, CNPh and CNN=CMe$_2$ moieties toward primary amine, since they are coordinated at the same metal center and are susceptible to nucleophilic attack by the primary amine.

The composition of the coordinated CNR and CNNR moieties provides a hint to the different reactivity towards amine. The Re–CN moiety attaches to a carbon atom in coordinated isocyanide (Re–CN–R), whereas the Re–CN moiety bonds to a nitrogen atom in *N*-isocyanoimine (Re–CN–NR) ligand. Due to the stronger electronegativity of a nitrogen atom in comparison to a carbon atom [13], the accelerating effect by an electron-attracting nitrogen atom increases the electrophilic character of the carbon atom linked to rhenium metal [11]. As a consequence, the *N*-isocyanoimine CNN=CMe$_2$ is preferentially susceptible to undergo nucleophilic attack by the amine.

2.6. Conclusion

The complex $ReBr(CO)_3$(CNR)(CNNPPh$_3$), prepared from the reaction of $ReBr(CO)_3$(CNR)(NCMe) with CNNPPh$_3$, readily reacts with ketones to form the complex $ReBr(CO)_3$(CNR)(CNN=CR′R″). Among the coordinated CO, CNPh and CNN=CMe$_2$ ligands at the rhenium centre of $ReBr(CO)_3$(CNPh)(CNN=CMe$_2$), the CNN = CMe$_2$ group is preferentially susceptible to nucleophilic attack by isopropylamine to form a carbene moiety. Subsequently, the CNPh could then react with an additional equivalent of amine to afford the biscarbene complex $ReBr(CO)_3${C(NHPr^i)(NHPh)}{C-(NHPr^i)(NHN=CMe$_2$)}.

3. Experimental

The complex $ReBr(CO)_4$(CNR) was prepared as previously reported [10]. Other reagents were purchased from commercial sources and were used as received. All manipulations were performed with standard Schlenk techniques. Chromatographic separations could be done in air if exposure is limited to a few hours. Solvents were dried by stirring over Na/benzophenone (diethyl ether) or CaH_2 (*n*-hexane, CH_2Cl_2, CH_3CN) and were freshly distilled prior to use. IR spectra were recorded on a Perkin–Elmer 882 IR spectrophotometer. NMR spectra were obtained on a Bruker AC-200 or an ACP-300 FT NMR spectrometer, and mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental analyzer. The ^{31}P chemical shifts are with reference to external 85% H_3PO_4.

3.1. Synthesis of $ReBr(CO)_3(CNPh)(CNNPPh_3)$ (**2a**)

A solution of $ReBr(CO)_4(CNPh)$ (300 mg, 0.624 mmol) in CH_2Cl_2 (100 ml) and acetonitrile (3 ml) was treated with a solution of Me_3NO (52 mg, 0.693 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred for 20 min at r.t. and filtered through a small silica gel column. The solvent was removed under vacuum to give $ReBr(CO)_3(CNPh)(NCMe)$. The latter was then stirred with $CNNPPh_3$ (188 mg, 0.622 mmol) in CH_2Cl_2 (100 ml) at r.t. for 12 h. After removal of solvent, the residue was chromatographed on a TLC plate with CH_2Cl_2 as eluent to give $ReBr(CO)_3(CNPh)(CNNPPh_3)$ (**2a**, 288 mg, 0.379 mmol) in a 61% yield. Anal. Calc. for $ReBrC_{29}H_{20}N_3O_3P$: C, 46.10; H, 2.67; N, 5.56. Found: C, 46.51; H, 2.82; N,5.19. IR (CH_2Cl_2): ν(CN) 2168 (br, w), ν(CO) 2031 (s), 1966 (s), 1916 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.72–7.19 (m, 5 H, 15 H, CNC_6H_5, $P(C_6H_5)_3$). ^{13}C-NMR ($CDCl_3$): δ 187.4, 187.3, 185.3 (CO), 145.9 (*C*NPh), 133.6–123.0 ($CN(C_6H_5)$, $P(C_6H_5)_3$), 92.6 (CNN). ^{31}P-NMR ($CDCl_3$): δ 32.36 (PPh_3).

3.2. Synthesis of complex $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**)

A solution of $ReBr(CO)_4(CNPr)$ (150 mg, 0.355 mmol) in CH_2Cl_2 (50 ml) and acetonitrile (1.5 ml) was treated with a solution of Me_3NO (28 mg, 0.373 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred for 20 min at r.t. and filtered through a small silica gel column. The solvent was removed under vacuum to give $ReBr(CO)_3(CNPr)(NCMe)$. The latter was then stirred with $CNNPPh_3$ (100 mg, 0.331 mmol) in CH_2Cl_2 (40 ml) at r.t. for 12 h. After removal of solvent, the residue was chromatographed on a TLC plate with CH_2Cl_2 as eluent to give $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**, 176 mg, 0.244 mmol) in a 74% yield. Anal. Calc. for $ReBrC_{26}H_{22}O_3N_3P$: C, 43.27; H, 3.08; N, 5.83. Found: C, 43.36; H, 2.92; N, 5.41. IR (CH_2Cl_2): ν(CN) 2207 (br, w), ν(CO) 2033 (s), 1959 (s), 1910 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.75–7.52 (m, 15 H, $P(C_6H_5)_3$), 3.58 (t, $J = 6.6$ Hz, 2 H, $CNCH_2$), 1.70 (m, 2 H, CH_2CH_3), 1.00 (t, $J = 7.4$ Hz, 3 H, CH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 187.9, 185.8 (CO), 133.6–123.4 ($P(C_6H_5)_3$), 94.0 (CNN), 45.7 ($CNCH_2$), 22.7 ($CNCH_2CH_2$), 10.90 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): δ 32.14 (PPh_3).

3.3. Reaction of $ReBr(CO)_3(CNR)(CNNPPh_3)$ with ketones

All compounds were prepared similarly and a typical preparation is listed here. $ReBr(CO)_3(CNPh)(CNN{=}C(CH_2)_5)$ (**3c**): a solution of $ReBr(CO)_3(CNPh)$-$(CNNPPh_3)$ (140 mg, 0.184 mmol) in CH_2Cl_2 (30 ml) was treated with cyclohexanone (1.5 ml) and several drops of HBF_4. The mixture was stirred for 10 min at r.t. After removal of the solvent, the residue was chromatographed on a TLC plate with a mixture of CH_2Cl_2 and *n*-hexane (70:30) as eluent to give $ReBr(CO)_3(CNPh)(CNN{=}C(CH_2)_5)$ (**3c**, 81 mg, 0.140 mmol) in a 76% yield. IR (CH_2Cl_2): ν(CN) 2181 (w, CNPh), 2152 (w, CNN), ν(CO) 2038 (s), 1985 (s), 1930 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.43 (s, 5 H, CNC_6H_5), 2.71, 2.40 (t, $J = 6.4$ Hz, t, $J = 6.3$ Hz, 2 H, 2 H, C_6H_{10}), 1.86–1.56 (m, 6 H, C_6H_{10}). ^{13}C-NMR ($CDCl_3$): δ 191.4, 186.3, 186.0, 183.9 (CO, NN=C), 143.5 (*C*NPh), 130.1, 129.6, 129.0, 126.9 (CNC_6H_5, CNN), 34.3, 32.4, 27.0, 26.4, 24.7 (C_6H_{10}).

The complex $ReBr(CO)_3(CNPr)(CNN{=}C(CH_2)_5)$ (**3d**) was obtained under similar reaction conditions in a 53% yield based on $ReBr(CO)_3(CNPr)(CNNPPh_3)$. Anal. Calc. for $ReBrC_{14}H_{17}O_3N_3$: C, 31.04; H, 3.17; N, 7.76. Found: C, 31.05; H, 3.32; N, 7.52. IR (CH_2Cl_2): ν(CN) 2211 (w, CNPr), 2153 (w, $CNNC(CH_2)_5$), ν(CO) 2038 (s), 1978 (s), 1924 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.71 (t, $J = 6.4$ Hz, 2 H, $CNCH_2$), 2.69, 2.40 (t, $J = 6.1$ Hz, t, $J = 6.1$ Hz, 2 H, 2 H, $NN{=}C(CH_2)_2$), 1.87–1.62 (m, 2 H, 6 H, $CNCH_2CH_2$, C_6H_{10}), 1.07 (t, $J = 7.4$ Hz, 3 H, CH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 191.1, 186.8, 186.3, 184.2 (CO, NN=C), 134.6 (*C*NPr), 129.7 (CNN), 46.0 ($CNCH_2$), 34.3, 32.3 ($NN{=}C(CH_2)_2$), 22.7 ($CNCH_2CH_2$), 10.9 ($CNCH_2CH_2CH_3$).

The complex $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) was obtained under similar reaction conditions in a 75% yield based on $ReBr(CO)_3(CNPh)(CNNPPh_3)$. Anal. Calc. for $ReBrC_{14}H_{11}O_3N_3$: C, 31.41; H, 2.07; N, 7.85. Found: C, 31.57; H, 2.07; N, 7.54. IR (CH_2Cl_2): ν(CN) 2182 (w, CNPh), 2152 (w, $CNNCMe_2$), ν(CO) 2039 (s), 1986 (s), 1931 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.43 (br, 5 H, C_6H_5), 2.33, 2.18 (s, 3 H, 3 H, $N{=}CMe_2$). ^{13}C-NMR ($CDCl_3$): δ 186.9, 186.3, 186.0, 183.9 (4 C, CO, NN=C), 143.7 (br, *C*NPh), 130.1, 129.6, 128.6, 126.9 (C_6H_5, CNN), 24.3, 22.5 (2 C, $N{=}CMe_2$).

The complex $ReBr(CO)_3(CNPr)(CNN{=}CMe_2)$ (**3b**) was obtained under similar reaction conditions in a 79% yield based on $ReBr(CO)_3(CNPr)(CNNPPh_3)$. IR ($CH_2Cl_2$): ν(CN) 2210 (w, CNPr), 2154 (w, CNN), ν(CO) 2039 (s), 1979 (s), 1924 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.71 (t, $J = 6.5$ Hz, 2 H, $CNCH_2$), 2.31, 2.17 (s, 3 H, 3 H, $N{=}CMe_2$), 1.80 (m, 2 H, $CNCH_2CH_2$), 1.06 (t, $J = 7.1$ Hz, 3 H, CH_2CH_3). ^{13}C-NMR ($CDCl_3$): δ 186.7, 186.2, 184.2 (s, 2:1:1, 4 C, CO, NN=C), 133.9 (t, 1:1:1, $J_{NH} = 20.3$ Hz, CNPr), 129.1 (CNN), 46.0 ($CNCH_2$), 22.7 ($CNCH_2CH_2$), 24.2, 22.4 (2 C, $N{=}C(CH_3)_2$), 10.9 ($CNCH_2CH_2CH_3$).

The complex $ReBr(CO)_3(CNPh)(CNN{=}C(CH_3)(Ph))$ (**3e**) was obtained under similar reaction conditions in a 67% yield based on $ReBr(CO)_3(CNPh)(CNNPPh_3)$. Anal. Calc. for $ReBrC_{19}H_{13}N_3O_3$: C, 38.20; H, 2.19; N, 7.03. Found: C, 37.91; H, 2.16; N, 6.70. IR (CH_2Cl_2):

ν(CN) 2179 (w, *C*NPh), 2144 (w, CNN), ν(CO) 2035 (s), 1985 (s), 1929 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 7.87–7.43 (m, 10 H, Ph), 2.69 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 186.4, 186.0, 183.8, 181.4 (4 C, CO, NN=C), 143.3 (br, CNPh), 131.6 (CNN), 133.6, 133.1, 130.1–126.5 (Ph), 18.7 (CH_3). Mass (FAB, ^{187}Re, ^{81}Br): m/z 599 (M^+), 571 (M^+–CO), 543 (M^+–2 CO).

3.4. Reaction of $ReBr(CO)_3(CNR)(CNN{=}CMe_2)$ with isopropylmine

A typical preparation is listed here. $ReBr(CO)_3(CNPh)\{(C(NHPr^i)(NHN{=}CMe_2)\}$ (**4a**): a solution of $ReBr(CO)_3(CNPh)(CN{=}NCMe_2)$ (120 mg, 0.224 mmol) in CH_2Cl_2 (20 ml) was treated with an excess of NH_2Pr^i (100 μl). The mixture was stirred for 30 min at r.t. After removal of solvent, the residue was recrystallized in a mixture of CH_2Cl_2 and *n*-hexane to afford $ReBr(CO)_3(CNPh)\{(C(NHPr^i)(NHN{=}CMe_2)\}$ (**4a**, 68 mg, 0.112 mmol) in a 53% yield. Anal. Calc. for $ReBrC_{17}H_{20}N_4O_3$: C, 34.35; H, 3.39; N, 9.42. Found: C, 34.91; H, 3.04; N, 9.06. IR (CH_2Cl_2): ν(CN) 2160 (w), ν(CO) 2026 (s), 1960 (s), 1901 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.73 (br, s, 1 H, CN(H)N), 7.97 (br, d, $J = 9.8$ Hz, 1 H, N(H)Pr^i), 7.38 (m, Ph), 4.38 (m, 1 H, NC*H*Me), 2.01, 1.99 (s, 3 H, 3 H, NC(CH_3)$_2$), 1.33, 1.29 (d, $J = 6.2$ Hz, d, $J = 6.2$ Hz, 3 H, 3 H, NHCH(CH_3)$_2$). ^{13}C-NMR ($CDCl_3$): δ 190.7, 190.0, 189.1 (1:2:1, 4 CO, N=*C*Me), 153.9 (C=N(H)), 149.8 (br, t, CNPh), 129.8, 129.6, 126.6 (Ph), 51.6 (N*C*HMe$_2$), 25.4, 17.2 (NC(*C*H_3)$_2$), 24.1 (NCH(*C*H_3)$_2$). Mass (FAB, ^{187}Re, ^{81}Br): m/z 596 (M^+), 568 (M^+–CO), 540 (M^+–2CO), 512 (M^+–3CO).

Complex $ReBr(CO)_3(CNPr)\{(C(NHPr^i)(NHN{=}CMe_2)\}$ (**4b**): complex **4b** was obtained in a 50% yield based on $ReBr(CO)_3(CNPr)(CNN{=}CMe_2)$ under similar reaction conditions as **4a**. IR (CH_2Cl_2): ν(CN) 2198 (w), ν(CO) 2028 (s), 1954 (s), 1899 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.72 (br, s, 1 H, CN(H)N), 7.91 (br, d, $J = 9.3$ Hz, 1 H, N(*H*)Pr^i), 4.32 (m, 1 H, NC*H*(CH_3)$_2$), 3.67 (t, $J = 6.6$ Hz, 2 H, CNCH_2CH$_2$CH$_3$), 2.01, 1.99 (s, 3 H, 3 H, NC(CH_3)$_2$), 1.77 (m, 2 H, CH$_2$CH_2CH$_3$), 1.30, 1.28 (d, $J = 6.4$ Hz, d, $J = 6.4$ Hz, 3 H, 3 H, NCH(CH_3)$_2$), 1.05 (t, $J = 7.4$ Hz, 3 H, CNCH$_2$CH$_2$CH_3). ^{13}C-NMR ($CDCl_3$): δ 190.9, 190.6, 189.4 (s, 1:2:1, 4 CO, NN=*C*(CH_3)), 153.7 (*C*N(H)), 140.0 (br, *C*NPr), 51.4 (N*C*H(CH_3)$_2$), 45.9 (CN*C*H$_2$CH$_2$CH$_3$), 25.4, 17.2 (NC(*C*H_3)$_2$), 24.1 (NCH(*C*H_3)$_2$), 22.9 (CNCH$_2$*C*H$_2$CH$_3$), 10.9 (CH$_2$CH$_2$*C*H$_3$).

3.5. Preparation of $ReBr(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ (5)

A solution of $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) (25 mg, 0.043 mmol) in CH_2Cl_2 (30 ml) was treated with excess NH_2Pr^i (1 ml). The mixture was stirred at r.t. for 1 day. The solvent was then removed under vacuum and the ^{1}H-NMR spectrum of the crude product showed that the yield of $ReBr(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**5**) was higher than 70%. The residue was chromatographed on a silica gel TLC plate with a mixture of CH_2Cl_2, *n*-hexane and acetonitrile (2:3:1) as eluent to give a colorless fraction (16 mg), which contained about 80% of **5**, a small amount of $ReBr(CO)_3(CNPh)\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**4a**), and some other impurities. Further recrystallisation of **5** led to an analytically impure sample which was still contaminated with these impurities. **5**: IR (CH_2Cl_2): ν(CO) 2018 (s), 1925 (s), 1871 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.45 (br, s, 1 H, CNHN), 8.51 (br, s, 1 H, CN*H*Ph), 7.86 (br, d, $J = 10.2$ Hz, 1 H, N*H*Pr^i), 7.45–7.04 (m, Ph), 6.30 (br, d, $J = 9.9$ Hz, 1 H, C(N*H*Pr^i)(NHPh)), 4.50 (m, 1 H, 1 H, NC*H*Me), 2.05, 1.95 (s, 3 H, 3 H, NC(CH_3)$_2$), 1.32, 1.28, 1.21, 1.04 (d, $J = 6.3$ Hz, d, $J = 6.5$ Hz, d, $J = 6.3$ Hz, d, $J = 6.5$ Hz, 3 H, 3 H, 3 H, 3 H, NHCH(CH_3)$_2$). Mass (FAB, ^{187}Re, ^{81}Br): m/z 655 (M^+), 627 (M^+–CO), 599 (M^+–2CO), 574 (M^+–Br), 546 (M^+–Br–CO).

3.6. In situ ^{1}H-NMR study on the interaction of complex 3a with isopropylamine

A solution of $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) (25 mg, 0.043 mmol) in $CDCl_3$ (0.5 ml) in an NMR tube was treated with excess NH_2Pr^i (0.05 ml). The reaction was monitored by ^{1}H-NMR spectroscopy at r.t. for 1 day. The complex $ReBr(CO)_3(CNPh)\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**4a**) was observed to be formed as the main product, and its concentration was slowly decreased with the concomitant formation of a new species assigned to the biscarbene complex $Re(CO)_3\{C(NHPr^i)(NHPh)\}\{C(NHPr^i)(NHN{=}CMe_2)\}$ (**5**). The yield of the latter appeared to be higher than 70% as estimated from the ^{1}H-NMR spectrum.

3.7. Crystallographic structure determination

Crystals of $ReBr(CO)_3(CNPr)(CNNPPh_3)$ (**2b**) and $ReBr(CO)_3(CNPh)(CNN{=}CMe_2)$ (**3a**) were grown from a mixture of CH_2Cl_2/*n*-hexane at −5°C. Specimens of suitable quality were mounted on glass capillaries and used for measurement of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo–K_α radiation ($\lambda = 0.710\ 69$ Å). Unit cell parameters were obtained by a least-squares fit to the automatically centered settings for 25 reflections. Intensity data were collected by using $\omega/2\theta$ scan mode. The systematic absences in the diffraction data of **2b** and **3a** unambiguously established

the space group as *Pbca* and $P2_1/n$, respectively. All intensity data were corrected for Lorentz-polarization and absorption (empirical Ψ corrections). The structure of **2b** was solved by direct methods SOLVER [14], and that of **3a** was solved by Patterson method. All remaining non-hydrogen atoms were located from the difference Fourier maps, and they were refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement factors. Calculations and full-matrix least-squares refinements were performed utilizing the NRCVAX program package [15].

4. Supplementary material

Tables of atomic co-ordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles for **2b** and **3a** (9 pages).

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