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Synthesis and reactivity of rhenium(I) isocyanide complexes. Crystal and molecular structures of $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ and $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$

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Abstract

The isocyanide complexes $ReBr(CO)_4(CNR)$ (**1a**, R = Pr; **1b**, R = ^{i}Pr; **1c**, R = Ph) are synthesized by reaction of $ReBr(CO)_5$ with phosphinimines via a deoxygenation mechanism. Complexes **1a** and **1b** react with an additional equivalent of $Ph_3P{=}NR$ to form the diisocyanide complexes $ReBr(CO)_3(CNR)_2$ (**2a**, R = Pr; **2b**, R = ^{i}Pr). The complex **1c** reacts with isopropylamine and propylamine in ether to afford the amidinium (carbene) complexes $ReBr(CO)_4\{C(NHPh)(NHR)\}$ (**4a**, R = ^{i}Pr; **4b**, R = Pr). However, **1c** does not react with tert-butylamine under the same reaction conditions. The reaction of **4a** with PPh_3 leads to the formation of the complexes $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$ (**5**). Complexes **4a** and **5** were crystallographically characterized. **4a**: $P2_1/c$, $a = 15.5557(15)$, $b = 6.5831(6)$, $c = 17.4149(9)$ Å, $\beta = 107.829(6)°$, $V = 1697.72(24)$ Å^3, $Z = 4$, $R = 0.031$, $R_w = 0.037$ for 2042 reflections with $F_o \geq 2\sigma(F_o)$. **5**: $P\bar{1}$, $a = 10.2318(17)$, $b = 33.638(3)$, $c = 10.1732(17)$ Å, $\alpha = 92.978(13)°$, $\beta = 119.612(8)°$, $\gamma = 91.627(10)°$, $V = 3034.1(8)$ Å^3, $Z = 4$, $R = 0.060$, $R_w = 0.079$ for 8349 reflections with $F_o \geq 2\sigma(F_o)$.

Introduction

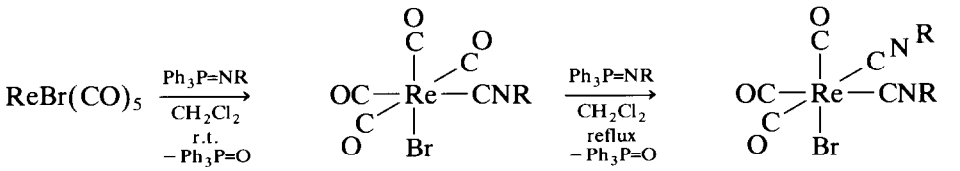
Most of the synthetic routes that lead to the preparation of metal isocyanide carbonyl complexes utilize the reaction of metal carbonyls with isocyanide ligands [1]. However, these reactions can result in a mixture of multisubstituted isocyanide units [1c–e]. Owing to the versatility of isocyanide complexes, it is of interest to find alternative synthetic routes to these compounds. Utilization of phosphinimines is one of the routes that have been employed for the synthesis of metal isocyanide complexes by generating the isocyanide ligand on the metal atom [2]. Phosphinimines are well known deoxygenating reagents [3]. Although there are many reported reactions between phosphinimines and organo-transition metal complexes [4], there are only a few examples that involve the deoxygenation by phosphinimines of carbonyl ligands to form isocyanide ligands [6a,b]. We therefore explored this sort of synthetic strategy as an alternative method to the preparation

of isocyanide complexes. We report the preparation of rhenium(I) isocyanide complexes by the ylide type reaction of $ReBr(CO)_5$ with phosphinimines and the reactions of these isocyanide complexes with primary amines.

Results and discussion

Reaction of $ReBr(CO)_5$ with $Ph_3P{=}NR$

Phosphinimine $Ph_3P{=}NR$ reacts with $ReBr(CO)_5$ in CH_2Cl_2 at room temperature to give the isocyanide complexes $ReBr(CO)_4(CNR)$ (**1a**, R = Pr; **1b**, R = ^{i}Pr) in high yield. Complexes **1a** and **1b** can further react with an additional equivalent of $Ph_3P{=}NR$ in refluxing CH_2Cl_2 to afford diisocyanide complex $ReBr(CO)_3(CNR)_2$ (**2a**, R = Pr; **2b**, R = ^{i}Pr) (eq. (1)). Complexes **2a** and **2b** can also be obtained directly from reaction of $ReBr(CO)_5$ with 2 equiv. of $Ph_3P{=}NR$. The monoisocyanide complex **1** was verified to be the intermediate in the preparation of **2** when this reaction was monitored by infrared spectroscopy.



(**1a**) R = Pr (93%)
(**1b**) R = ^{i}Pr (92%)

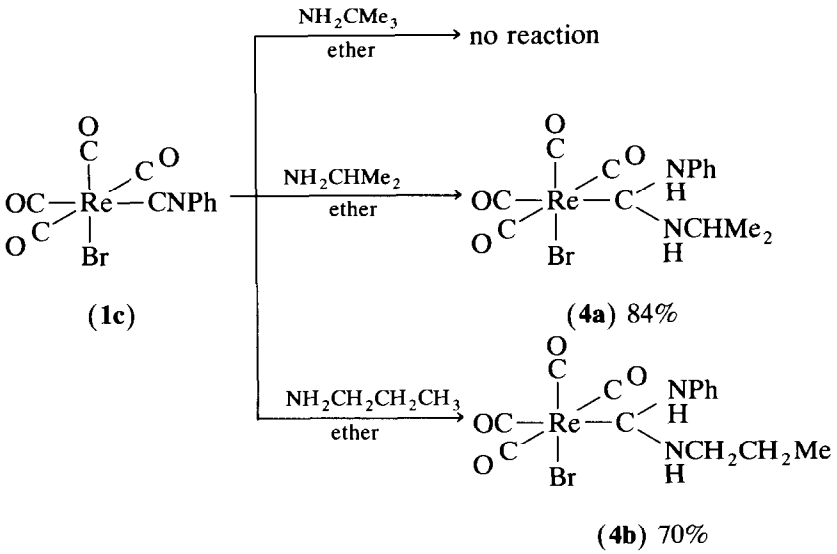
(**2a**) R = Pr (73%)
(**2b**) R = ^{i}Pr (76%)

(1)

$Ph_3P{=}NPh$, a weaker nucleophilic reagent than $Ph_3P{=}NPr$, reacts with $ReBr(CO)_5$ in refluxing CH_2Cl_2 to form monoisocyanide complex $ReBr(CO)_4(CNPh)$ (**1c**) in high yield (95%). In contrast to **1a** and **1b**, the complex **1c** does not react with excess $Ph_3P{=}NPh$ to produce diisocyanide product under the same reaction conditions. Therefore, **1c** could be easily isolated as the monoisocyanide complex in very high yield.

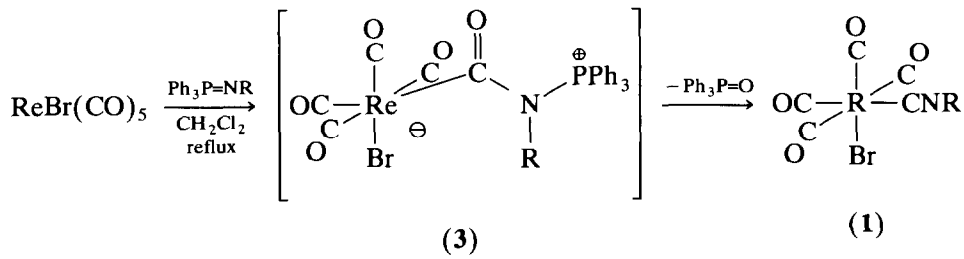
These results reveal that the ylide type reaction of the deoxygenation of the $ReBr(CO)_5$ by phosphinimines can provide an appropriate, alternative route to the synthesis of the mono- and diisocyanide rhenium complexes. Treichel *et al.* had previously reported the preparation of the rhenium(I) isocyanide complexes [1d]. It is interesting to compare the reactivity of $ReBr(CO)_5$ between the direct substitution of CO by isocyanide and the deoxygenation of CO by phosphinimines. They observed that $ReBr(CO)_5$ undergoes direct carbonyl replacement by isocyanide reagents to afford a series of di- or multi-isocyanide complexes $ReBr(CO)_{5-n}L_n$ ($n \geqslant 2$) instead of the monoisocyanide complex $ReBr(CO)_4(CNR)$, and that the monoisocyanide complex $ReBr(CO)_4(CNR)$ was obtained by the reaction of $Re_2Br_2(CO)_8$ with isocyanide. However, our results indicate that the monoisocyanide complexes can be produced easily by the reaction of $ReBr(CO)_5$ with phosphinimine, and the experimental manipulations also have the advantage of avoiding the preparative inconvenience and the notorious odor of isocyanide reagents.

In addition to complex **1**, the above reactions also produced $Ph_3P{=}O$ as a by-product, isolated and characterized by comparison of its spectroscopic data with



Scheme 1.

that of an authentic compound [5]. The mechanism of this reaction is likely to be as follows (eq. 2):



(2)

The rhenium complex initially undergoes nucleophilic attack by phosphinimine at the carbonyl carbon to form the intermediate (**3**). Phosphinimines have previously been proposed to deoxygenate carbonyl ligands via this type of intermediate [6]. The intermediate **3** then eliminates $Ph_3P{=}O$ to generate the isocyanide complex **1**.

Reaction of $ReBr(CO)_4(CNPh)$ with primary amine in ether

Treatment of $ReBr(CO)_4(CNPh)$ with isopropylamine or propylamine in ether produces the amidinium (carbene) complexes $ReBr(CO)_4\{C(NHPh)(NHR)\}$ (**4a**, R = ^{i}Pr; **4b**, R = Pr) (Scheme 1).

These complexes were characterized by spectroscopic methods. Complex **4a** has also been crystallographically characterized and the spectroscopic data are consistent with its formulation. A drawing of the molecular structure is shown in Fig. 1. In this complex, pseudo-octahedral geometry is observed around the Re atom. The Br atom is in the *cis* position of the carbene (amidinium) group. The C5–N1 and C5–N2 bonds show partial double bonds (1.328, 1.330 Å, respectively). The three

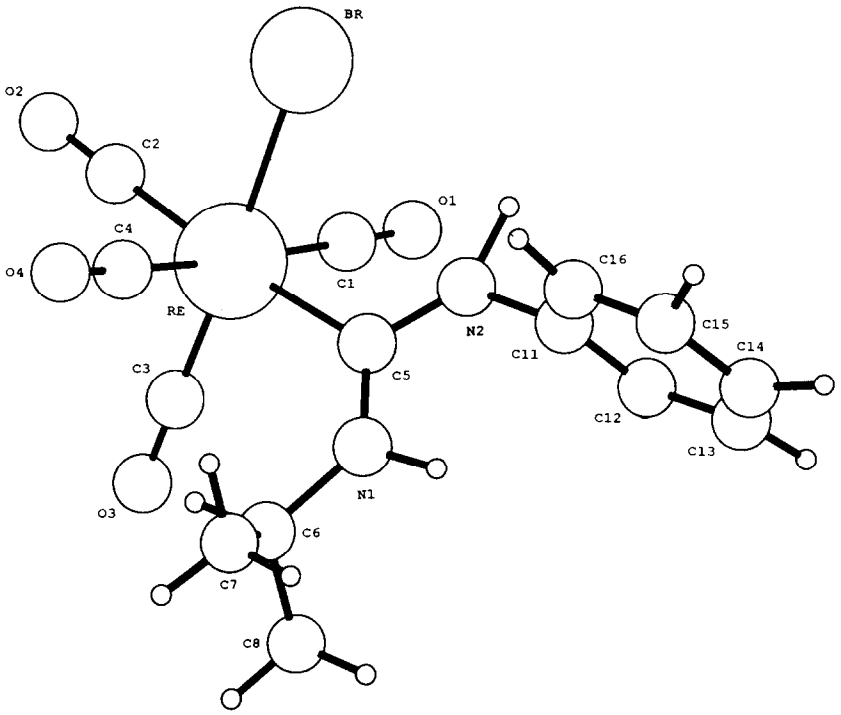


Fig. 1. Molecular structure of $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$.

CO ligands *cis* to the Br group have slightly longer Re–C(CO) distances (1.997, 1.987, 1.961 Å) than the *trans* CO ligand (1.901 Å). This is likely due to the Br ligand which tends to labilize the *cis* positions [7]. ^{1}H NMR analysis of **4a** showed that the resonance of *H*N(2) (δ 8.82) appeared much more downfield than that of *H*N(1) (δ 6.35), as expected from the electron withdrawing effect of the phenyl group.

Treatment of **1c** with tert-butylamine in ether at room temperature or under refluxing conditions gave no noticeable change of the reactants to the expected product; only starting materials were recovered. This lack of reactivity is presumably due to the steric hindrance of the bulky tert-butyl group.

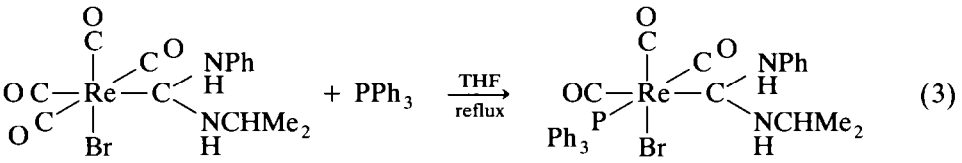
We found that **1a** and **1b**, containing the aliphatic isocyanide group, failed to react with primary amine to produce the carbene complexes. This may be attributed to the subtle electronic effect. The electron releasing aliphatic group makes the isocyanide more electron-rich, consequently, the nucleophilic attack of the amine on the carbon of the isocyanide ligands becomes difficult. Crociani [8] has studied the factors affecting the reactivity of isocyanide complexes with respect to the nature of the coordinated isocyanide. He observed that an electron-attracting group effectively increases the electrophilic character of the carbon atom of the isocyanide ligand linked to metal. He also showed that there exists a noticeable difference in the reactivity between the phenyl and cyclohexyl isocyanides.

Angilici [9] has compared the relative reactivities of CO and CNR ligands with CH_3NH_2 in complexes which contained both ligands. He found that as the C–O force constant decreases, amine addition to CO becomes thermodynamically less

favorable and amine addition to $CNCH_3$ predominates. We observed that the isocyanide ligand in $ReBr(CO)_4(CNPh)$ exhibits a pronounced tendency to undergo nucleophilic attack by amines to give the carbene complexes.

Reaction of $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ with phosphine

$ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ reacts with triphenylphosphine in refluxing THF to give $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$ (**5**) in which one CO ligand both *cis* to the carbene group and *cis* to the Br ligand was replaced by phosphine.



(**4a**) (**5**) (3)

The structure of **5** is intriguing. Although carbene and phosphine in complex **5** are bulky ligands, complex **5** is a facial isomer with these two bulky ligands in the *cis* orientation. The electronic factor is likely more predominant than the steric factor since the facial isomer is preferred electronically. The dissociation of CO both *cis* to Br and *cis* to carbene is presumably easier due to the *cis* labilizing ability of Br and carbene ligands and thereby exhibits a pronounced tendency to be substituted by a phosphine ligand to afford a facial isomer **5**. ^1H NMR analysis of **5** revealed that the resonance peaks of the two methyl groups are separated up to 0.24 ppm (δ 1.12 and δ 0.88, respectively). The two methyl groups of carbene appear to encounter different chemical environments possibly because of the interaction with the bulky PPh_3 ligand.

*Crystal and molecular structures of **4a** and **5***

ORTEP drawings of **4a** and **5** are given in Figs. 1 and 2, and pertinent crystallographic details are set out in Tables 1–5. The complex **4a** crystallizes in the space group $P2_1/c$. Pseudo-octahedral geometry is observed around the Re atom. C(5) of the carbene ligand appears as an sp^2 hybrid with a distorted trigonal planar arrangement. The bond angle of Re–C(5)–N(1) (128.2(7)°) appears larger than that of Re–C(5)–N(2) (117.1(7)°) and N(1)–C(5)–N(2) (114.7(9)°) due to the steric hindrance of the bulkier phenyl group. The Br and the carbene (amidinium) groups are *cis* to each other. C(5)–N(1) and C(5)–N(2) show partial double-bond character (1.328(12), 1.330(13) Å, respectively). The dihedral angle of Br–Re–C(5)–N(2) is 37.5(4)°. The three CO ligands *cis* to the bromide ligand have slightly longer Re–C(CO) distances (1.997(11), 1.989(12), 1.961(11) Å) than the *trans* CO ligand (1.901(12) Å). This is likely due to the *cis* labilization effect of the Br ligand. The complex **5** crystallized as two crystallographically independent but structurally similar molecules. The pseudo-octahedral geometry is also observed around the Re atom. The three CO ligands are arranged in a facial configuration, with a somewhat longer Re–C distance for the CO *trans* to the carbene ligand. The carbene ligand shows a similar bond character to that of the complex **4a**. The C(3)–Re(1)–C(4) bond angle, 175.2(4)°, is deviated from 180°, and this may be

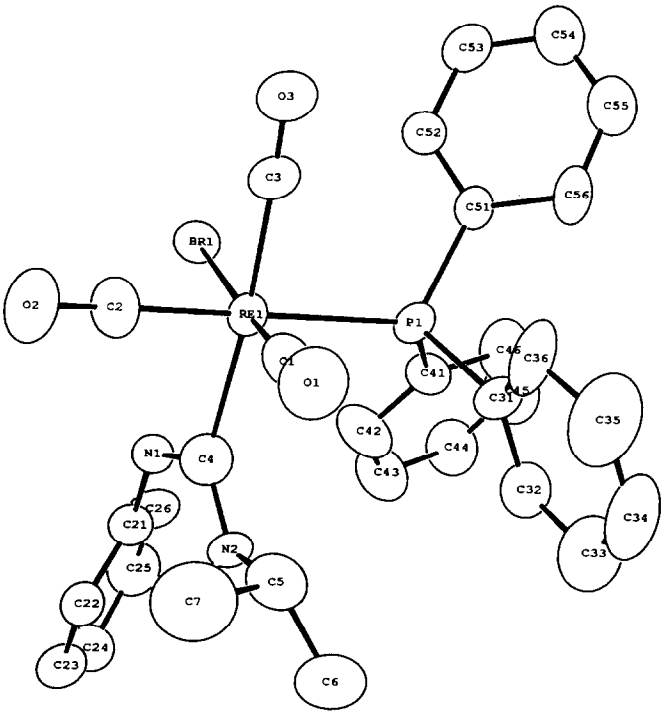


Fig. 2. Molecular structure for one molecule of two chemically similar but crystallographically independent molecules of $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$.

attributed to the steric factor, whereby the bulky ligands, triphenylphosphine and carbene, stay as far apart as possible.

Experimental

General data

The complexes $ReBr(CO)_5$, $Ph_3P{=}NPh$, $Ph_3P{=}N^tBu$, $Ph_3P{=}NPr$ were prepared by literature procedures [10–12]. Other reagents were purchased from commercial sources and were used as received. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by stirring over Na/benzophenone (tetrahydrofuran, ether) or CaH_2 (hexane, CH_2Cl_2) and were freshly distilled prior to use. Chromatography was performed under nitrogen, using a Florisil column. IR spectra were recorded on a Perkin–Elmer 882 infrared spectrophotometer. NMR spectra were obtained on a Brucker MSL-200 or an AC-200 FT-NMR spectrometer, and electron impact (EI) 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 referenced with respect to external 85% H_3PO_4.

Reaction of $ReBr(CO)_5$ with $Ph_3P{=}NPr$

The complex $ReBr(CO)_5$ (252 mg, 0.62 mmol) and $Ph_3P{=}NPr$ (204 mg, 0.640 mmol) were stirred in CH_2Cl_2 (60 mL) at room temperature for 1 h. The solvent

Table 1
Crystal and intensity collection data for $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ and $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$

Molecular formula	$C_{14}H_{14}BrN_2O_4Re$	$C_{30}H_{29}BrN_3O_3PRe$
Mol. wt.	540.39	776.66
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	15.5557(15)	10.2318(17)
b (Å)	6.5831(6)	33.638(3)
c (Å)	17.4149(9)	10.1732(17)
α (deg)	–	92.978(13)
β (deg)	107.829(6)	119.612(8)
γ (deg)	–	91.627(10)
V (Å^3)	1697.72(24)	3034.1(8)
ρ(calc.) (g cm^{-3})	2.114	1.700
Z	4	4
Crystal dimensions (mm)	$0.14\times0.13\times0.06$	$0.50\times0.41\times0.25$
Absolute coefficient μ (Mo-K_α) (cm^{-1})	96.0	98.8
Temperature	Room temperature	Room temperature
Radiation	Mo-K_α $\lambda = 0.70930$ Å	Cu-K_α $\lambda = 1.54056$ Å
2θ range	50°	120°
Scan type	$2\theta-\omega$	$2\theta-\omega$
No. of reflections	3094	9054
No. of observed reflections	2042 ($>2.0\sigma$)	8349 ($>2.0\sigma$)
Variables	199	703
R	0.031	0.060
R_W	0.033	0.079
S	1.11	3.05
ΔF (e/Å^3)	<0.710	<3.240
$(\Delta/\sigma)_{max}$	0.042	0.0253

was removed under vacuum and the residue was chromatographed on Florisil. Elution with CH_2Cl_2/hexane (50:100) afforded a colorless fraction, from which microcrystalline $ReBr(CO)_4(CNPr)$ (**1a**) was obtained in 93% yield (258 mg, 0.58 mmol) after evaporation of the solvent. Further elution with THF/CH_2Cl_2 (15:100) afforded a colorless fraction, from which microcrystalline $Ph_3P{=}O$ was obtained after evaporation of the solvent. $Ph_3P{=}O$: m/z (EI) = 287 (M^+). ^{31}P NMR ($CDCl_3$): δ 29.5 ppm. Literature value [5]: δ 29.3.

1a: Anal. Found: C, 21.57; H, 1.50. $C_8H_7BrNO_4Re$ calc.: C, 21.47; H, 1.57%. IR (CH_2Cl_2): ν (CN) 2221m, ν(CO) 2113m, 2020vs, 1958s cm^{-1}. EI (Re^{187}, Br^{81}): m/z 449 (M^+) and fragments corresponding to loss of four COs. ^1H NMR ($CDCl_3$): δ 3.79 (t, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.11 (t, 3H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 182.4, 181.2, 180.2 (CO), 129.4 (CN), 22.6 (CH_2), 10.9 (CH_3) ppm.

Complex $ReBr(CO)_4(CN^iPr)$ (**1b**) was obtained under similar reaction conditions as **1a** (241 mg, 0.54 mmol, 92%).

1b: Anal. Found: C, 21.60; H, 1.59. $C_8H_7BrNO_4Re$ calc.: C, 21.47; H, 1.57%. IR (CH_2Cl_2): ν(CN) 2213m, ν(CO) 2112m, 2020vs, 1956s cm^{-1}. EI, (Re^{187}, Br^{81}): m/z 449 (M^+).

Table 2
Atomic coordinates and isotropic thermal parameters (Å^2) for ReBr(CO)$_4${C(NHPh)(NHCHMe$_2$)}

Atom	x	y	z	B_{eq} [a]
Re	0.27009(3)	0.11437(6)	0.24340(2)	2.55(2)
Br	0.19150(9)	0.42895(19)	0.28738(7)	4.45(6)
N1	0.2915(6)	0.2636(14)	0.0752(4)	3.5(4)
N2	0.1629(5)	0.3603(15)	0.0968(5)	3.5(4)
O1	0.0795(6)	−0.0862(14)	0.1800(5)	5.5(5)
O2	0.2997(6)	−0.0621(15)	0.4143(4)	6.2(5)
O3	0.3563(6)	−0.2669(13)	0.2008(5)	5.1(5)
O4	0.4506(6)	0.3532(15)	0.3073(5)	6.2(5)
C1	0.1485(8)	−0.0157(16)	0.2028(6)	3.2(5)
C2	0.2884(7)	0.0000(18)	0.3512(6)	3.7(5)
C3	0.3249(7)	−0.1229(18)	0.2171(6)	3.4(5)
C4	0.3853(8)	0.2682(18)	0.2830(6)	4.0(6)
C5	0.2411(7)	0.2623(16)	0.1245(6)	2.9(5)
C6	0.3816(7)	0.1726(17)	0.0877(6)	3.5(5)
C7	0.4499(8)	0.3369(22)	0.0901(8)	5.5(7)
C8	0.3764(9)	0.0142(22)	0.0245(8)	5.7(8)
C11	0.1330(7)	0.4755(17)	0.0217(6)	3.0(5)
C12	0.0821(7)	0.3853(17)	−0.0467(6)	3.6(5)
C13	0.0517(8)	0.4911(21)	−0.1173(6)	4.3(6)
C14	0.0729(8)	0.6903(22)	−0.1184(7)	4.8(7)
C15	0.1247(10)	0.7872(17)	−0.0500(8)	4.9(7)
C16	0.1541(8)	0.6785(17)	0.0218(6)	3.9(6)
H1	0.263(6)	0.331(14)	0.023(5)	3.6(23)
H2	0.105(10)	0.412(23)	0.103(80	15.4(50)
H6	0.409(5)	0.114(13)	0.141(4)	1.9(18)
H7A	0.514(7)	0.293(14)	0.106(5)	2.9(25)
H7B	0.461(6)	0.452(13)	0.129(5)	5.8(23)
H7C	0.435(6)	0.410(15)	0.038(5)	2.7(26)
H8A	0.438(7)	−0.053(18)	0.033(6)	5.4(31)
H8B	0.387(9)	0.100(20)	−0.016(7)	5.6(44)
H8C	0.339(7)	−0.109(18)	0.025(6)	5.6(36)
H12	0.062(5)	0.241(13)	−0.047(4)	1.6(19)
H13	0.008(7)	0.422(15)	−0.163(5)	5.4(26)
H14	0.042(6)	0.786(13)	−0.161(5)	1.0(21)
H15	0.114(7)	0.936(15)	−0.049(5)	3.7(25)
H16	0.186(7)	0.759(16)	0.068(5)	2.3(32)

[a] $B_{eq} = 8/3\ \pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Reaction of ReBr(CO)$_5$ with Ph$_3$P=NPh

The complex ReBr(CO)$_5$ (101 mg, 0.25 mmol) and Ph$_3$P=NPh (87 mg, 0.25 mmol) were stirred in CH_2Cl_2 (50 mL) under gentle reflux for 23 h. The solvent was removed under vacuum and the residue was chromatographed on Florisil. Elution with CH_2Cl_2/hexane (50:100) afforded a colorless fraction, from which microcrystalline ReBr(CO)$_4$(CNPh) (**2c**) was obtained in 95% yield (116 mg, 0.24 mmol) after evaporation of the solvent.

1c: Anal. Found: C, 27.32; H, 1.15. $C_{11}H_5BrNO_4Re$ calc.: C, 27.44; H, 1.04%. IR (CH_2Cl_2): ν(CN) 2190m, ν(CO) = 2109s, 2025vs, 1963s cm^{-1}. EI (Re^{187}, Br^{81}): m/z 481 (M^+) and fragments corresponding to loss of four ligands. ^{1}H NMR (acetone-d_6): δ 7.69–7.68, 7.60–7.57 (m, 5H, Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 182.3, 180.8, 179.9 (CO), 138.2 (CN), 132.1, 130.9, 129.8, 128.5, 127.0 (Ph) ppm.

Table 3
Atomic coordinates and isotropic thermal parameters (Å^2) for $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$

	x	y	z	B_{eq} [a]
Re1	0.89542(4)	0.15006(1)	0.04969(4)	2.49(2)
Re2	1.54159(4)	0.64986(1)	0.90199(4)	2.61(2)
Br1	0.88453(10)	0.07961(3)	0.15520(11)	3.46(4)
Br2	1.64816(11)	0.57917(3)	0.88729(10)	3.72(4)
P1	0.73201(23)	0.11839(5)	−0.21630(22)	2.59(9)
P2	1.28138(23)	0.61858(6)	0.73418(24)	2.83(10)
N1	1.1791(7)	0.1039(2)	0.1485(8)	2.9(3)
N2	1.1807(8)	0.1488(2)	−0.0063(8)	2.8(3)
N11	1.4960(8)	0.6499(2)	1.1956(8)	3.2(3)
N12	1.6455(8)	0.6035(2)	1.1842(7)	2.6(3)
O1	0.8798(9)	0.2336(2)	−0.0582(9)	5.3(5)
O2	1.0942(10)	0.1894(2)	0.3711(8)	6.2(5)
O3	0.6130(8)	0.1702(2)	0.0666(9)	5.3(4)
O11	1.8643(9)	0.6843(2)	1.1160(9)	6.3(4)
O12	1.4218(9)	0.7320(2)	0.8874(9)	5.4(5)
O13	1.5569(10)	0.6736(3)	0.6195(9)	6.0(5)
C1	0.8890(10)	0.2028(2)	−0.0212(10)	3.6(4)
C2	1.0206(11)	0.1742(2)	0.2522(11)	3.9(5)
C3	0.7136(11)	0.1633(3)	0.0581(11)	4.0(5)
C4	1.1094(10)	0.1345(2)	0.0608(10)	4.4(5)
C5	1.1475(12)	0.1853(3)	−0.0823(13)	4.6(5)
C6	1.2063(14)	0.1831(4)	−0.1950(16)	6.4(8)
C7	1.2342(20)	0.2197(3)	0.0400(20)	8.0(12)
C11	1.7402(10)	0.6715(3)	1.0299(10)	3.8(4)
C12	1.4688(11)	0.7010(2)	0.8980(9)	3.3(4)
C13	1.5529(10)	0.6636(3)	0.7249(11)	3.6(4)
C14	1.5589(9)	0.6332(2)	1.1182(9)	4.2(4)
C15	1.4052(11)	0.6839(3)	1.1615(12)	3.9(5)
C16	1.5090(16)	0.7210(3)	1.2399(16)	6.5(8)
C17	1.2914(14)	0.6781(3)	1.2138(15)	5.6(7)
C21	1.3031(10)	0.0833(3)	0.1604(10)	3.5(5)
C22	1.4408(10)	0.1027(3)	0.2073(10)	3.7(4)
C23	1.5631(12)	0.0799(3)	0.2218(11)	4.2(5)
C24	1.5405(11)	0.0397(3)	0.1816(12)	4.7(5)
C25	1.3988(13)	0.0201(3)	0.1397(13)	4.9(6)
C26	1.2843(12)	0.0413(3)	0.1298(12)	4.3(6)
C31	0.7255(10)	0.1524(2)	−0.3560(10)	3.2(4)
C32	0.7989(11)	0.1449(3)	−0.4352(11)	4.1(5)
C33	0.7973(17)	0.1726(4)	−0.5360(16)	7.1(9)
C34	0.7128(18)	0.2036(4)	−0.5608(13)	7.8(9)
C35	0.6396(21)	0.2118(4)	−0.4813(17)	8.2(11)
C36	0.6473(15)	0.1847(3)	−0.3750(10)	5.3(7)
C41	0.7828(10)	0.0704(2)	−0.2739(10)	3.4(4)
C42	0.9264(12)	0.0588(3)	−0.1981(14)	5.3(6)
C43	0.9685(12)	0.0261(3)	−0.2523(13)	5.3(6)
C44	0.8578(13)	0.0016(3)	−0.3735(13)	4.8(5)
C45	0.7125(16)	0.0120(4)	−0.4467(15)	6.5(7)
C46	0.6684(14)	0.0482(3)	−0.4005(12)	5.2(6)
C51	0.5359(9)	0.1068(2)	−0.2688(9)	2.7(4)
C52	0.5000(10)	0.0892(2)	−0.1698(9)	3.2(4)
C53	0.3538(12)	0.0776(3)	−0.2087(12)	4.9(6)

Table 3 (continued)

	x	y	z	B_{eq} [a]
C54	0.2404(13)	0.0841(4)	−0.3490(13)	5.5(6)
C55	0.2695(12)	0.1018(3)	−0.4505(11)	4.8(5)
C56	0.4165(11)	0.1145(3)	−0.4147(9)	4.0(5)
C61	1.6638(8)	0.5824(2)	1.3145(9)	2.6(4)
C62	1.6310(12)	0.5420(3)	1.2891(12)	4.3(5)
C63	1.6423(13)	0.5200(3)	1.4084(12)	4.6(6)
C64	1.6896(12)	0.5413(3)	1.5473(11)	4.3(5)
C65	1.7237(11)	0.5815(3)	1.5690(11)	4.4(5)
C66	1.7154(10)	0.6029(2)	1.4559(9)	3.1(4)
C71	1.2276(10)	0.6054(2)	0.5336(10)	3.2(4)
C72	1.3334(11)	0.5892(2)	0.5037(9)	3.5(5)
C73	1.3021(11)	0.5766(3)	0.3638(12)	4.3(5)
C74	1.1533(11)	0.5804(3)	0.2400(11)	4.4(5)
C75	1.0428(10)	0.5983(3)	0.2640(9)	4.0(4)
C76	1.0837(9)	0.6106(2)	0.4123(11)	3.6(4)
C81	1.1372(10)	0.6534(2)	0.7170(10)	3.3(4)
C82	1.0615(11)	0.6459(3)	0.7963(14)	4.8(6)
C83	0.9567(13)	0.6736(5)	0.7903(15)	6.8(7)
C84	0.9314(16)	0.7072(4)	0.7003(17)	7.1(8)
C85	1.0079(16)	0.7128(3)	0.6236(16)	6.8(8)
C86	1.1145(13)	0.6850(3)	0.6360(13)	5.1(6)
C91	1.2247(10)	0.5716(3)	0.7845(10)	3.4(4)
C92	1.3045(15)	0.5609(3)	0.9297(12)	5.4(7)
C93	1.2512(16)	0.5256(3)	0.9679(13)	6.1(8)
C94	1.1311(12)	0.5022(3)	0.8603(13)	4.3(5)
C95	1.0537(13)	0.5135(3)	0.7152(14)	6.1(6)
C96	1.0990(13)	0.5481(3)	0.6819(15)	6.0(7)

[a] $B_{eq} = 8/3\ \pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

The preparation of $ReBr(CO)_3(CNPr)_2$

The reaction of **1a** with one equivalent of $Ph_3P{=}NPr$ in refluxing CH_2Cl_2 gave $ReBr(CO)_3(CNPr)_2$ (**2a**). After working up, **2a** was purified by chromatography on Florisil (238 mg, 0.49 mmol, 73%). **2a** was also obtained by reaction of $ReBr(CO)_5$ with 2 equiv. of $Ph_3P{=}NPr$.

2a: Anal. Found: C, 27.06; H, 272. $C_{11}H_{14}BrN_2O_3Re$ calc.: C, 27.05; H, 2.87%. IR (CH_2Cl_2): ν(CN) 2219, 2197m, ν(CO) 2040s, 1979s, 1924s cm^{-1}. EI (Re^{187}, Br^{81}): m/z 490 (M^+) and fragments corresponding to loss of three ligands. ^1H NMR ($CDCl_3$): δ 3.72 (t, 4H, CH_2), 1.81 (m, 4H, CH_2), 1.08 (t, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 186.29, 184.25 (CO), 134.5 (t, CN, ^1J(CN) = 20.6 Hz), 46.01 (CH_2), 22.74 (CH_2), 10.97 (CH_3) ppm.

Complex $ReBr(CO)_3(CN^iPr)_2$ (**2b**) was obtained under similar reaction conditions as **2a** (65 mg, 0.13 mmol, 76%).

2b: Anal. Found: C, 27.03; H, 2.67. $C_{11}H_{14}BrN_2O_3Re$ calc.: C, 27.05; H, 2.87%. IR (CH_2Cl_2): ν(CN) 2210, 2188m, ν(CO) = 2039s, 1976s, 1925s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.15 (m, 2H, CH), 1.47 (d, 6H, CH_3) ppm.

Reaction of $ReBr(CO)_4(CNPh)$ with amine in ether

The complex $ReBr(CO)_4(CNPh)$ (122 mg, 0.25 mmol) and excess isopropylamine were stirred in ether (50 mL) at room temperature for 1.5 h. After removal of solvent, the white residue was recrystallized in CH_2Cl_2/hexane to afford

Table 4
Selected bond distances (Å) and angles (°) for $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$

Re–Br	2.6350(12)	Re–C(1)	1.997(11)
Re–C(2)	1.961(11)	Re–C(3)	1.901(12)
Re–C(4)	1.989(12)	Re–C(5)	2.206(10)
N(1)–C(5)	1.328(12)	N(1)–C(6)	1.479(14)
C(11)–C(12)	1.350(15)	C(11)–C(16)	1.376(16)
N(2)–C(5)	1.330(13)	C(12)–C(13)	1.364(15)
N(2)–C(11)	1.460(12)	C(13)–C(14)	1.354(20)
O(1)–C(1)	1.125(14)	O(2)–C(2)	1.135(13)
C(14)–C(15)	1.374(20)	O(3)–C(3)	1.142(15)
O(4)–C(4)	1.123(15)	C(15)–C(16)	1.391(16)
C(6)–C(7)	1.508(17)	C(6)–C(8)	1.500(17)
Br–Re–C(1)	88.1(3)	Br–Re–C(2)	88.2(3)
Br–Re–C(3)	176.2(3)	Br–Re–C(4)	87.0(4)
Br–Re–C(5)	86.9(3)	C(1)–Re–C(2)	91.1(4)
C(1)–Re–C(3)	90.4(4)	C(1)–Re–C(4)	174.7(5)
C(1)–Re–C(5)	87.6(4)	C(2)–Re–C(3)	88.3(4)
C(2)–Re–C(4)	90.7(4)	C(2)–Re–C(5)	174.9(4)
C(3)–Re–C(4)	94.6(5)	N(2)–C(11)–C(12)	120.2(10)
C(3)–Re–C(5)	96.6(4)	N(2)–C(11)–C(16)	119.5(9)
C(4)–Re–C(5)	90.2(4)	C(5)–N(1)–C(6)	128.5(8)
C(12)–C(11)–C(16)	120.2(9)	C(5)–N(2)–C(11)	125.6(8)
C(11)–C(12)–C(13)	121.2(10)	Re–C(1)–O(1)	178.9(10)
C(12)–C(13)–C(14)	119.3(11)	Re–C(2)–O(2)	178.5(11)
Re–C(3)–O(3)	178.8(10)	Re–C(4)–O(4)	178.3(10)
C(13)–C(14)–C(15)	121.2(10)	Re–C(5)–N(1)	128.2(7)
Re–C(5)–N(2)	117.1(7)	N(1)–C(5)–N(2)	114.7(9)
C(14)–C(15)–C(16)	119.0(11)	N(1)–C(6)–C(7)	110.0(9)
N(1)–C(6)–C(8)	109.7(9)	C(11)–C(16)–C(15)	119.1(10)
C(7)–C(6)–C(8)	113.5(10)		

$ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ (**4a**). Complex **4a**, further purified by chromatography on Florisil with hexane/CH_2Cl_2 (50:100) (115 mg, 0.21 mmol, 84%).

4a: Anal. Found: C, 31.26; H, 2.50. $C_{14}H_{14}BrN_2O_4Re$ calc.: C, 31.12; H, 2.61%. IR (CH_2Cl_2): ν(CO) 2104m, 2001vs, 1931s cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.82 (s, 1H, N*H*), 7.52–7.28, 7.18–7.14 (m, 5H, ph), 6.35 (d, 1H, N*H*, $J = 10.14$ Hz), 4.27 (m, 1H, C*H*), 1.21 (d, 6H, CH_3, $J = 6.43$ Hz). ^{13}C NMR ($CDCl_3$): δ 191.88, 186.19, 185.88, 185.61 (*C* (amidinium) and *C*O ligands), 135.88, 130.44, 128.17, 125.85 (Ph), 52.72 (*C*H), 23.67 (2 CH_3) ppm.

Complex **4b** was obtained under similar reaction conditions in 70% yield based on $ReBr(CO)_4(CNPh)$.

4b: Anal. Found: C, 31.14; H, 2.42. $C_{14}H_{14}BrN_2O_4Re$ calc.: C, 31.12; H, 2.61%. IR (CH_2Cl_2): ν(CO) 2101m, 1994vs, 1930s cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.95 (s, 1H, N*H*), 7.51–7.39, 7.20–7.16 (m, 5H, ph), 6.53 (b, 1H, N*H*), 3.52 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 0.90 (t, 3H, CH_3) ppm.

Reaction of $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ with phosphine

The complex $ReBr(CO)_4\{C(NHPh)(NHCHMe_2)\}$ (**4a**) (220 mg, 0.41 mmol) and triphenylphosphine (109 mg, 0.41 mmol) were stirred in refluxing THF (50 mL) for 5 h. After removal of solvent, the residue was chromatographed on Florisil with

Table 5
Selected bond distances (Å) and angles (°) for $ReBr(CO)_3(PPh)_3\{C(NHPh)(NHCHMe_2)\}$

Re(1)–Br(1)	2.6736(9)	Re(1)–P(1)	2.5260(20)
Re(1)–C(1)	1.940(8)	Re(1)–C(2)	1.924(9)
Re(1)–C(3)	1.967(9)	Re(1)–C(4)	2.215(8)
Re(2)–Br(2)	2.6715(10)	Re(2)–P(2)	2.5045(21)
Re(2)–C(11)	1.886(8)	Re(2)–C(12)	1.888(8)
Re(2)–C(13)	1.940(9)	Re(2)–C(14)	2.221(8)
N(1)–C(4)	1.367(11)	N(1)–C(21)	1.418(11)
N(2)–C(4)	1.319(11)	N(2)–C(5)	1.443(11)
N(11)–C(14)	1.352(11)	N(11)–C(15)	1.440(11)
N(12)–C(14)	1.328(10)	N(12)–C(61)	1.468(10)
Br(1)–Re(1)–P(1)	88.69(5)	Br(1)–Re(1)–C(1)	174.4(3)
Br(1)–Re(1)–C(2)	91.3(3)	Br(1)–Re(1)–C(3)	88.9(3)
Br(1)–Re(1)–C(4)	88.49(22)	P(1)–Re(1)–C(1)	92.6(3)
P(1)–Re(1)–C(2)	179.8(3)	P(1)–Re(1)–C(3)	89.8(3)
P(1)–Re(1)–C(4)	94.24(21)	C(1)–Re(1)–C(2)	87.4(4)
C(1)–Re(1)–C(3)	85.6(4)	C(1)–Re(1)–C(4)	96.9(4)
C(2)–Re(1)–C(3)	90.5(4)	C(2)–Re(1)–C(4)	85.5(4)
C(3)–Re(1)–C(4)	175.2(4)	Br(2)–Re(2)–P(2)	88.19(5)
Br(2)–Re(2)–C(11)	89.8(3)	Br(2)–Re(2)–C(12)	174.93(24)
Br(2)–Re(2)–C(13)	89.5(3)	Br(2)–Re(2)–C(14)	86.89(20)
P(2)–Re(2)–C(11)	177.9(3)	P(2)–Re(2)–C(12)	92.2(3)
P(2)–Re(2)–C(13)	90.1(3)	P(2)–Re(2)–C(14)	95.78(22)
C(11)–Re(2)–C(12)	89.9(4)	C(11)–Re(2)–C(13)	90.5(4)
C(11)–Re(2)–C(14)	83.5(4)	C(12)–Re(2)–C(13)	85.5(4)
C(12)–Re(2)–C(14)	98.1(3)	C(13)–Re(2)–C(14)	173.0(3)
C(4)–N(1)–C(21)	128.7(7)	C(4)–N(2)–C(5)	124.5(8)
C(14)–N(11)–C(15)	128.8(7)	C(14)–N(12)–C(61)	129.4(7)
Re(1)–C(4)–N(1)	115.5(6)	Re(1)–C(4)–N(2)	131.2(6)
N(1)–C(4)–N(2)	113.3(7)	Re(2)–C(14)–N(11)	128.8(6)
Re(2)–C(14)–N(12)	116.7(6)	N(11)–C(14)–N(12)	114.5(7)

30% CH_2Cl_2/hexane to give $ReBr(CO)_3(PPh_3)\{C(NHPh)(NHCHMe_2)\}$ (**5**) (172 mg, 0.22 mmol, 54%).

5: Anal. Found: C, 48.36; H, 3.68. $C_{31}H_{29}BrN_2O_3PRe$ calc.: C, 48.06; H, 3.75%. IR (THF): ν(CO) 2024s, 1933s, 1885s cm^{-1}. EI: m/z 774 (M^+). ^1H NMR ($CDCl_3$): δ 8.83 (s, 1H, N*H*), 7.57–6.85 (m, 20H, 4ph), 6.30 (d, 1H, N*H*, $J = 9.5$ Hz), 4.20 (m, 1H, C*H*), 1.12 (d, 3H, CH_3, $J = 6.37$ Hz), 0.88 (d, 3H, CH_3, $J = 6.37$ Hz). ^{13}C NMR ($CDCl_3$): δ 199.32 (CO, J(PC) = 9.8 Hz), 193.60 (CO, J(PC) = 7.1 Hz), 191.95 (CO, J(PC) = 7.1 Hz), 190.63 (C, J(PC) = 63.6 Hz), 136.68–125.22 (Ph), 51.57 (*C*H), 24.56 (*C*H_3), 23.01 (*C*H_3) ppm. ^{31}P NMR ($CDCl_3$): δ 8.99 ppm.

Crystallographic structure determination

Crystallographic data for the two complexes are shown in Table 1. Specimens of suitable quality were mounted in a glass capillary and used for measurement of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf–Norius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.70930$ Å) with θ–2θ scan mode for **4a**. Diffraction measurements were made on a Rigaku AFC5R diffractometer using graphite-monochromated Cu-K_α radiation ($\lambda = 1.54056$ Å) with θ–2θ scan mode for **5**.

Unit cell was determined from centering 25 reflections in the 2θ range 19.42–34.44° and systematic absences unambiguously established the space group as $P2_1/c$ for **4a**. The centrosymmetric space group was initially assumed and later confirmed by the results of refinement for **5**. Absorption corrections according to ψ scans of three reflections were made. The structure was solved by locating the Re atom from a Patterson map. All remaining non-hydrogen atoms were located from the difference Fourier map, and they were included in the final refinement cycle and refined by full-matrix least squares. All the data processing was carried out on a Microvax 3600 using the NRCC SDP program.

Supplementary material. For **4a** and **5**, tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (12 pages); tables of structure factors (39 pages) are available from the authors.

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