

Synthesis of nitrosyl rhenium(I) complexes bearing bidentate ligands

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Abstract

The reaction of $[\text{ReCl}(\mu\text{-Cl})(\text{CO})(\text{NO})]_2$ (**2**) (obtained from $[\text{ReCl}(\mu\text{-Cl})(\text{CO})_2(\text{NO})]$ and cyclooctene (COE)) with 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine leads to $\text{ReCl}_2(\text{CO})_2\text{L}(\text{NO})$ complexes ($\text{L} = 2,2'$ -bipyridine (**3**), 4,4'-dimethyl-2,2'-bipyridine (**4**)) with *trans* chloride substituents. The reaction of $[\text{ReCl}(\mu\text{-Cl})(\text{CO})_2(\text{NO})]_2$ (**1**) with THF produces racemic $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ (**5**). The Re–THF bond in **5** is labile enough to provide a primary coordination site for a bidentate ligand attack. The reaction of **2** with bpy proceeds with regioselective Re–Cl cleavage *trans* to the CO ligand and affords the ionic $[\text{ReCl}(\text{CO})_2(\text{bpy})(\text{NO})][\text{ReCl}_2(\text{CO})_2(\text{NO})]$ complex **6** or, when a stoichiometric amount of NaBF_4 is present, $[\text{ReCl}(\text{CO})_2(\text{bpy})(\text{NO})][\text{BF}_4]$ (**7**). The reaction of **2** with 1,2-bis(diphenylphosphino)methane (dppm) gives *cis,trans*- $[\text{ReCl}_2(\eta^1\text{-dppm})_2(\text{CO})(\text{NO})]$ (**8**) while the transformation with 1,2-bis(diphenylphosphino)ethene (dppee), and NaBF_4 , yields an ionic $[\text{ReCl}(\text{NO})(\text{dppee})_2][\text{BF}_4]$ compound **9**. The reaction of racemic *trans*-1,2-bis(dimethylphosphino)cyclopentane (dmpe) with **5** proceeds with loss of the THF molecule and of one CO group, affording a diastereomeric mixture of $\text{ReCl}_2(\text{CO})(\text{dmpe})(\text{NO})$ (**10**). The compounds **2**, **4**, **5**, **6**, **8**, **9** and **10** were characterized by X-ray diffraction studies. Crystal data: **2**, monoclinic, space group $P2_1/c$, $a = 9.471(5)$, $b = 10.646(6)$, $c = 12.599(7)$ Å, $\beta = 99.78(2)^\circ$, $V = 1251.8(12)$ Å³, $Z = 2$; **4**, monoclinic, space group $C2/m$, $a = 13.472(4)$, $b = 21.717(7)$, $c = 6.491(2)$ Å, $\beta = 105.33(2)^\circ$, $V = 1831.7(9)$ Å³, $Z = 4$; **5**, monoclinic, space group $P2_1/n$, $a = 6.114(3)$, $b = 18.443(12)$, $c = 9.954(5)$ Å, $\beta = 96.09(2)^\circ$, $V = 1116.2(10)$ Å³, $Z = 4$; **6**, triclinic, space group $P\bar{1}$, $a = 8.894(2)$, $b = 10.376(2)$, $c = 14.660(4)$ Å, $\alpha = 97.62(2)^\circ$, $\beta = 97.46(2)^\circ$, $\gamma = 102.67(2)^\circ$, $V = 1290.4(6)$ Å³, $Z = 2$; **8**, monoclinic, space group $P2_1/n$, $a = 10.029(3)$, $b = 30.364(9)$, $c = 16.487(3)$ Å, $\beta = 98.10(2)^\circ$, $V = 4971(2)$ Å³, $Z = 4$; **9**, trigonal, space group $P\bar{3}$, $a = 20.648(7)$, $c = 11.326(4)$ Å, $V = 4182(3)$ Å³, $Z = 4$; **10**, tetragonal, space group $Fdd2$, $a = 14.265(3)$, $b = 50.190(10)$, $c = 9.217(2)$ Å, $V = 6599(2)$ Å³, $Z = 16$.

Keywords: Ligand replacement; Coordination compounds; Bidentate N, P donors; Rhenium nitrosyl complexes; Stereoisomers

1. Introduction

Recently the chemistry of transition metal nitrosyl complexes has attracted growing interest [1–5], in particular in the context of Lewis acid applications of coordination compounds [6–11]. Several features of the NO ligand are important for its preferential choice in this respect: the small steric demand, the strong π accepting power and the high *trans* effect and influence. Appropriate $d^6\{\text{Re-NO}\}$ complexes indeed display Lewis acidic properties. In these compounds the metal center is usually associated with monodentate P donors [12–20] or cyclopentadienyl derivatives [21–23]. Many Lewis acidic coordination compounds however contain bidentate P or N donors, but the number of

reported nitrosyl Re(I) species with this type of ligand is rather limited [20,24,25]. This prompted us to explore new synthetic routes to obtain bidentate P and N donor substituted complexes with the relatively hard {Re–NO} fragment [26].

In 1971, Uguagliati and coworkers [20,27,28] described the synthesis of the first halogen bridged carbonyl rhenium nitrosyl complex $[\text{ReCl}(\mu\text{-Cl})(\text{CO})_2(\text{NO})]_2$ (**1**). The investigation of its reactivity towards various ligands showed that mostly harder σ donor ligands L like pyridine, 4-picoline, 3,4-lutidine, etc. cause splitting of the halide bridges of **1** forming $\text{ReCl}_2(\text{CO})_2\text{L}(\text{NO})$ molecules [27,28]. With a π ligand like cyclooctene (COE), however, the halide bridge is preserved and CO substitution takes place producing an $[\text{ReCl}(\mu\text{-Cl})(\text{CO})(\text{COE})(\text{NO})]_2$ species [20] (**2**). In view of the above mentioned goal to prepare rhenium nitrosyl compounds with bidentate ligands, it seemed appropri-

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ate to pursue a stepwise synthetic strategy starting from complexes with easily exchangeable ligands like **2** or from $\text{ReCl}_2(\text{CO})_2(\text{NO})\text{L}$ species with a labile Re–L bond (e.g. L = THF).

2. Experimental section

2.1. General considerations

All preparations were carried out under an atmosphere of dry nitrogen by conventional Schlenk techniques. All solvents were purified by usual methods. *trans*-1,2-bis(Dimethylphosphine)cyclopentane was prepared from *trans*-1,2-bis(dichlorophosphine)cyclopentane [29] and treated as for the analogous synthesis of 1,2-bis(dimethylphosphine)ethane [30]. The crude product was distilled over a 20 cm Vigreux column at 0.01 mbar/35 °C (yield 65%). The compounds 1,2-bis(diphenylphosphine)ethane (dppe), 1,2-bis(diphenylphosphine)ethene (dppee), 1,2-bis(diphenylphosphine)methane (dppm), cyclooctene (COE) and 2,2'-bipyridine (bpy) were used as purchased from Fluka. The complex **1** [12,19] was prepared as described previously. Elemental analyses were carried out by the Analytical Department of the Organic Laboratory of Zürich University. IR spectra were recorded on a Biorad FTS-45 instrument. Mass spectra were run on a Finnigan MAT-8230 mass spectrometer with an EI source (70 eV). ^1H and ^{13}C NMR spectra were obtained on a Varian Gemini 200 spectrometer operating at 200 and 50.3 MHz respectively. ^{31}P NMR spectra were measured on a Gemini 300 at 121 MHz.

2.2. $[\text{ReCl}(\mu\text{-Cl})(\text{CO})(\text{COE})(\text{NO})]_2$ (**2**)

A solution of 340 mg (0.49 mmol) $[\text{ReCl}(\mu\text{-Cl})(\text{CO})_2(\text{NO})]_2$ (**1**) and 1 ml cyclooctene in 20 ml toluene was heated under reflux for 8 h. The solution was concentrated in vacuo to ca. 10 ml and 10 ml pentane was added. On standing at –30 °C overnight yellow prisms separated. Yield 295 mg (70%). IR (KBr pellets, cm^{-1}): 2924w, 2855w, 2066s, 1776s, 1467w, 1447w, 1181w, 520w, 475w, 443w. ^1H NMR (CDCl_3): δ 1.34–1.80 (m, 8H, $-\text{CH}_2-$); 1.82–2.08 (m, 2H, $-\text{CH}_2-\text{CH}=\text{CH}-$); 2.45–2.60 (m, 1H, $-\text{CH}_2-\text{CH}=\text{CH}-$); 2.72–2.85 (m, 1H, $-\text{CH}_2-\text{CH}=\text{CH}-$); 3.94–4.09 (m, 1H, $-\text{CH}=\text{CH}-$); 4.85–5.02 (m, 1H, $-\text{CH}=\text{CH}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CDCl_3): δ 25.83 (s, $-\text{CH}_2-$); 26.04 (s, $-\text{CH}_2-$); 26.21 (s, $-\text{CH}_2-$); 28.37 (s, $-\text{CH}_2-$); 32.19 (s, $-\text{CH}_2-$); 86.98 (s, $-\text{CH}=\text{CH}-$); 88.03 (s, $-\text{CH}=\text{CH}-$); 189.86 (s, CO). Anal. Found: C, 25.60; H, 3.38; N, 3.30; Re, 43.53. $\text{C}_{18}\text{H}_{28}\text{Cl}_4\text{N}_2\text{O}_4\text{Re}_2$ (850.42) Calc.: C, 25.42; H, 3.29; N, 3.29; Re, 43.79%.

2.3. $\text{trans-}[\text{ReCl}_2(\text{CO})(\text{bpy})(\text{NO})]$ (**3**)

A solution of 416 mg (0.49 mmol) $[\text{ReCl}(\mu\text{-Cl})(\text{CO})(\text{COE})(\text{NO})]_2$ (**2**) in 20 ml dichloromethane and 180 mg (1.15 mmol) 2,2'-bipyridine was stirred for 1 h at RT and three days at 40 °C (reflux). During this time the mixture turned red and a dark red powder precipitated. This powder was collected, washed with diethylether (2×5 ml) and recrystallized from dimethylformamide/acetone. Analytically pure prisms can alternatively be obtained by slow evaporation of a dimethylformamide solution of **3**. Yield 220 mg (51%). IR (KBr pellets, cm^{-1}): 3110w, 3079w, 2923w, 2848w, 1967s, 1725s, 1604m, 1494w, 1469w, 1442m, 1310w, 1244w, 1108w, 1067w, 1049w, 775m, 730w, 653w, 596w, 508w. Anal. Found: C, 28.64; H, 1.78; N, 8.49. $\text{C}_{11}\text{H}_8\text{Cl}_2\text{ON}_3\text{Re}$ (455.23) Calc.: C, 29.02; H, 1.75; N, 9.22%.

2.4. $\text{trans-}[\text{ReCl}_2(\text{CO})(4,4'\text{-dimethyl-bipyridine})(\text{NO})]$ (**4**)

Similar treatment as for **3** however starting from 200 mg (1.08 mmol) 4,4'-dimethyl-2,2'-bipyridine. The obtained red powder can be purified by recrystallization from hot acetonitrile (5 ml). Yield 270 mg (55%). IR (KBr pellets, cm^{-1}): 3071w, 3035w, 2961w, 2927w, 2855w, 1973s, 1718s, 1618m, 1558w, 1486w, 1442w, 1418w, 1304w, 1244w, 1138w, 1034w, 897w, 848m, 564w, 522w, 505w, 472w, 416w. ^1H NMR (acetone- d_6): δ 2.65 (s, 3H, CH_3-); 2.71 (s, 3H, CH_3-); 7.67 (m, 1H, $\text{H}^{3\text{bpy}}$); 7.74 (m, 1H, $\text{H}^{3\text{bpy}}$); 8.55–8.66 (m, 4H, $\text{H}^{5,6\text{bpy}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, acetone- d_6): δ 21.38 (s, CH_3); 21.83 (s, CH_3); 75.59 (s), 75.85 (s), 128.38 (s), 148.04 (s), 151.12 (s): all CH^{bpy} ; 153.12 (s), 154.14 (s), 154.80 (s), 155.54 (s), all C^{bpy} ; 214.82 (s, CO). FAB-MS (CH_3CN): m/z 499 (M^+ , 18); 471 (M^+-CO , 79); 464 (M^+-Cl , 22); 436 ($\text{M}^+-\text{CO}-\text{Cl}$, 20). Anal. Found: C, 34.15; H, 2.90; N, 11.30; Re, 37.14. $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_3\text{O}_3\text{Re} \cdot \text{CH}_3\text{CN}$ (540.26) Calc.: C, 33.41; H, 2.78; N, 10.36; Re, 37.29%.

2.5. $[\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})]$ (**5**)

A solution of 200 mg (0.29 mmol) **1** in 10 ml THF was stirred at RT for 30 min. The reaction mixture was reduced to 2 ml and crystallization from THF/hexane at –30 °C gave moderately air stable yellow plates of **5**. Yield 228 mg (95%). IR (KBr pellets, cm^{-1}): 3003w, 2994w, 2108s, 2021s, 1779s, 1017w, 868w, 594w, 481w, 421w, 358w. ^1H NMR (C_6D_6): δ 0.92–0.99 (m, 4H, $-\text{O}-\text{CH}_2-$); 3.66–3.73 (m, 4H, $-\text{CH}_2-\text{CH}_2-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, C_6D_6): δ 25.48 (s, $-\text{O}-\text{CH}_2-$); 76.05 (s, $-\text{CH}_2-\text{CH}_2-$); 185.39 (s, CO); 186.76 (s, CO). MS (EI): m/z 415 (M^+), 387 (M^+-CO), 356 (M^+-2CO). Anal. Found: C, 17.38; H, 2.28; N, 3.21;

Table 1
IR data for 1–10 (KBr pellets, cm^{-1})

Compound	$\nu(\text{CO})$	$\nu(\text{NO})$
1	2108, 2048	1807
2	2066	1776
3	1967	1725
4	1973	1718
5	2103, 2029	1773
6	2113, 2051 ^a	1807 ^a
	2094, 2020 ^b	1766 ^b
7	2115, 2052	1818
8	2002	1734
9	—	1714
10	2019	1746
	2009	1711

^a Cation. ^b Anion.

Re, 44.41. $\text{C}_6\text{H}_8\text{Cl}_2\text{NO}_3\text{Re}$ (415.17) Calc.: C, 17.35; H, 1.92; N, 3.37; Re, 44.85%.

2.6. $[\text{ReCl}(\text{CO})_2(\text{bpy})(\text{NO})][\text{ReCl}_3(\text{CO})_2(\text{NO})]$ (6)

A solution of 200 mg (0.29 mmol) **5** and 100 mg (0.64 mmol) 2,2'-bipyridine in 15 ml THF was heated under reflux. After 1 h the yellow solution became dark orange and later a yellow powder precipitated. After three days the reaction mixture was concentrated to 2 ml. A yellow powder was formed, which was filtered off and washed with pentane (2×10 ml). Recrystallization from a mixture of 3 ml dichloromethane, a few drops of acetone and 2 ml pentane at $+5^\circ\text{C}$ gave yellow prisms of **6**. Yield 137 mg (56%). IR (KBr pellets, cm^{-1}): 3120w, 3092w, 3064w, 2113s, 2094s, 2052s, 2020s, 1807s, 1766s, 1739s, 1612w, 1605m, 1500m, 1454m, 1447m, 1322w, 1246w, 1160w, 1109w, 1077w, 1039w, 772m, 726w, 649w, 621w, 548m, 520w,

480m. ^1H NMR (acetone- d_6): δ 8.10 (m, 2H, $\text{H}5^{\text{bpy}}$); 8.71 (m, 2H, $\text{H}4^{\text{bpy}}$); 9.11 (m, 2H, $\text{H}3^{\text{bpy}}$); 9.62 (m, 2H, $\text{H}6^{\text{bpy}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, acetone- d_6): δ 126.5 (s), 130.1 (s), 134.1 (s), 144.2 (s), 156.6 (s): bpy; 186.7 (s, CO_{anion}); 188.8 (s, $\text{CO}_{\text{cation}}$). Anal. Found: C, 19.73; H, 1.17; N, 6.47; Cl, 16.58. $\text{C}_{14}\text{H}_8\text{Cl}_4\text{N}_4\text{O}_6\text{Re}_2$ (842.37) Calc.: C, 19.96; H, 0.95; N, 6.64; Cl, 16.83%.

2.7. $[\text{ReCl}(\text{CO})_2(\text{bpy})(\text{NO})][\text{BF}_4]$ (7)

A solution of 300 mg (0.43 mmol) **5**, 101 mg (0.88 mmol) NaBF_4 and 143 mg (0.91 mmol) 2,2'-bipyridine in 20 ml THF was stirred at RT for 2 h and then heated under reflux. An orange precipitate was formed after 20 h. It was filtered off, washed with diethylether (2×5 ml), dried in vacuo and extracted with 20 ml acetonitrile. Addition of diethylether and crystallization at $+5^\circ\text{C}$ caused precipitation of orange plates of **7**, which were washed with diethylether and dried in vacuo. Yield 107 mg (45%). IR (KBr pellets, cm^{-1}): 3126w, 3094w, 3070w, 3044w, 2927w, 2852w, 2115s, 2052s, 1818s, 1609m, 1505w, 1478m, 1447m, 1326w, 1247w, 1109m, 1070s, 1049s, 1024m, 902w, 779m, 730w, 494w. ^1H NMR (acetone- d_6): δ 8.10 (m, 2H, $\text{H}5^{\text{bpy}}$); 8.71 (m, 2H, $\text{H}4^{\text{bpy}}$); 9.11 (m, 2H, $\text{H}4^{\text{bpy}}$); 9.62 (m, 2H, $\text{H}6^{\text{bpy}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, acetone- d_6): δ 126.5 (s), 130.1 (s), 134.1 (s), 144.2 (s), 156.6 (s): C^{bpy} ; 188.8 (s, CO). Anal. Found: C, 25.99; H, 1.69; N, 7.69; Re, 33.25. $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_3\text{ClF}_4\text{BrRe}$ (550.60) Calc.: C, 26.17; H, 1.45; N, 7.63; Re, 33.82%.

2.8. *cis,trans*- $[\text{ReCl}_2(\text{dppm})_2(\text{CO})(\text{NO})]$ (8)

A solution of 310 mg (0.45 mmol) of **1** was heated at 80°C in acetonitrile for 10 min. After cooling to RT,

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **2**

Atom	x	y	z	U_{eq}^a
Re(1)	504(1)	334(1)	3635(1)	26(1)
Cl(1)	—739(4)	2273(4)	3735(4)	44(2)
Cl(2)	1469(4)	639(3)	5590(3)	34(1)
O(1)	—1338(14)	—79(12)	1378(11)	57(5)
O(2)	2027(15)	—2059(11)	3746(9)	54(5)
N(1)	1427(15)	—1098(12)	3609(10)	36(5)
C(1)	—619(17)	79(15)	2201(17)	47(7)
C(2)	1796(17)	1259(16)	2400(14)	42(6)
C(3)	2457(17)	1488(12)	3460(11)	29(5)
C(4)	3876(18)	911(19)	3902(14)	53(7)
C(5)	5120(18)	1804(21)	3728(15)	58(8)
C(6)	5092(28)	2097(30)	2562(19)	105(12)
C(7)	4887(30)	1290(33)	1717(23)	123(16)
C(8)	3470(19)	997(21)	1043(15)	57(7)
C(9)	2356(19)	398(18)	1636(14)	50(6)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **4**

Atom	x	y	z	U_{eq}^a
Re(1)	0	3344(1)	0	33(1)
Cl(1)	1647(2)	3247(2)	−781(4)	49(1)
N(1)	−509(6)	2553(4)	−2040(11)	33(2)
O(1)	−765(10)	4317(5)	−3384(19)	76(4)
Cl(10)	−480(9)	3954(5)	−2099(19)	46(4)
Cl(1)	−1044(8)	2583(5)	−4107(14)	39(3)
Cl(2)	−1394(8)	2074(5)	−5337(14)	40(3)
Cl(3)	−1196(9)	1489(6)	−4419(15)	44(3)
Cl(4)	−635(9)	1463(5)	2280(15)	41(3)
Cl(5)	−306(7)	1988(4)	−1146(12)	34(3)
Cl(6)	−1565(13)	923(7)	−5691(21)	66(5)
N(1S)	1281(31)	0	161(54)	121(16)
Cl(1S)	2176(20)	0	761(38)	71(9)
Cl(2S)	3267(19)	0	1411(46)	83(10)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

366 mg (0.95 mmol) of 1,2-bis(diphenylphosphine)-methane was added and the mixture was stirred for 1 h at RT and heated at reflux for 14 h. Then the volume of the resulting suspension was reduced to 10 ml in vacuo and the precipitate was filtered off and washed with diethylether (2×10 ml). Suitable crystals for an X-ray diffraction study were obtained by cooling a dichloromethane/pentane solution of **8** to $+5^\circ\text{C}$. Yield 520 mg (48%). IR (KBr pellets, cm^{-1}): 3055w, 3022w, 2920w, 2856w, 2002s, 1992s, 1734s, 1587w, 1574w, 1483m, 1436m, 1375w, 1191w, 1157w, 1181w, 1097m, 1028w, 999w, 738s, 694s, 655w, 557m, 504m, 490m. ^1H NMR (CDCl_3): δ 3.48 (m, 2H, $\text{P}-\text{CH}_2-\text{P}$); 4.05 (m, 2H, $\text{P}-\text{CH}_2-\text{P}$); 7.09–7.7 (m, H_{ph} , 40H). ^{13}C (^1H) NMR (50.3 MHz, CDCl_3): δ 20.58 (m, $\text{P}-\text{CH}_2-\text{P}$), 128.2–130.9 (m, C_{ph}); 197.8 (s, CO). ^{31}P (^1H) NMR (CDCl_3): δ 1.70 (t-virt, $^2J_{\text{pp}} = 20$ Hz); -28.50 (t-virt, $^2J_{\text{pp}} = 20$ Hz). Anal. Found: C, 56.53; H, 4.32; N, 1.56; Re, 16.75. $\text{C}_{51}\text{H}_{44}\text{P}_4\text{Cl}_2\text{NO}_2\text{Re}$ (1083.90) Calc.: C, 56.51; H, 4.05; N, 1.29; Re, 17.17%.

2.9. $[\text{ReCl}(\text{NO})(\text{dppee})_2][\text{BF}_4]$ (**9**)

A suspension of 200 mg (0.29 mmol) **1** in 15 ml THF was heated under reflux for 10 min. The starting material had then dissolved and $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ had formed (IR monitoring). After cooling to RT and addition of 67 mg (0.6 mmol) NaBF_4 , the solution was stirred for 10 min and 510 mg (1.2 mmol) 1,2-bis(diphenylphosphino)ethene was added. The reaction mixture was again heated under reflux for 48 h. The reaction mixture was allowed to cool to RT and the yellowish precipitate was filtered off, washed with diethylether (2×10 ml) and dried in vacuo. Extraction with 40 ml acetonitrile and recrystallization from hot acetonitrile afforded white/yellow prisms of **9**. Yield 230 mg (70%). IR (KBr pellets, cm^{-1}): 3053w, 3024w, 2926w, 2847w, 1714s, 1483w, 1434m, 1212brs, 1122shs, 1082s, 1061s, 910m, 805m, 749m, 695s, 564s, 517m, 475w, 456w. ^1H NMR (300 MHz, CD_3CN): δ 6.92–7.02 (m, 16H, H_{ph}); 7.22–7.33 (m, 16H, H_{ph}); 7.41–7.48 (m, 8H, $\text{H}_{\text{p-ph}}$);

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **5**

Atom	x	y	z	U_{eq}^a
Re(1)	326(1)	1658(1)	3121(1)	35(1)
Cl(1)	−1529(6)	1770(2)	881(3)	57(1)
Cl(2)	−2851(6)	1033(2)	3783(4)	62(1)
O(2)	4049(17)	2533(6)	2237(13)	70(5)
O(1)	−1671(17)	3110(6)	3976(10)	61(4)
O(3)	2639(21)	1413(7)	5927(11)	72(5)
O(4)	1379(16)	617(5)	2437(8)	47(3)
Cl(1)	−911(25)	2574(8)	3668(14)	48(5)
Cl(2)	2693(20)	2169(6)	2593(12)	32(4)
N(1)	1778(18)	1504(7)	4847(13)	53(4)
Cl(4)	2634(25)	506(9)	1269(14)	55(5)
Cl(5)	3571(27)	−249(9)	1422(18)	66(6)
Cl(6)	2277(32)	−634(9)	2392(18)	68(7)
Cl(7)	1622(32)	−36(9)	3281(17)	73(7)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

7.88–8.08 (m, 4H, P–CH=CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 30.0 (s). Anal. Found: C, 54.11; H, 4.33; N, 1.24; Re, 16.23. $\text{C}_{52}\text{H}_{44}\text{ClNO}_4\text{P}_4\text{Re}$ (1130.92) Calc.: C, 55.22; H, 3.89; N, 1.23; Re, 16.46%.

2.10. *rac*-[ReCl₂(dmpc)(CO)(NO)] (10)

A solution of 300 mg (0.44 mmol) **1** in 20 ml acetonitrile was stirred at RT for 20 min. Then 175 mg (1.10 mmol) (\pm)-trans-1,2-bis(dimethylphosphino)cyclopentane was added. The yellow solution gradually turned orange with evolution of CO. After 30 h the solvent was removed in vacuo and the crude product purified by recrystallization from dichloromethane/pentane (3:1) at -30°C . Repeated recrystallization gave orange/yellow plates of the isomeric mixture of **10** in analytically pure form. Yield 350 mg (80%). IR (KBr pellets, cm^{-1}): 2972w, 2947w, 2908w, 2866w, 2017s/2009s, 1747s/1711s, 1447w, 1415w, 1306w, 1284w, 1137w, 1070w, 948m, 921m, 887w, 847w, 754w, 700w, 527w, 462w, 445w. ^1H

NMR (CDCl_3): δ 1.40–1.80 (m, 12H, PMe); 2.25–2.35 (m, 8H, CH/CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CDCl_3): δ 2.00–14.53 (PMe); 21.9–23.2, 30.4–31.4 (m, CH₂); 45.9–52.1 (CH); 196.48 (d \times d, $^2J_{\text{PC}} = 4.6$ Hz, $^2J_{\text{PC}} = 8.9$ Hz, CO); 198.29 (d \times d, $^2J_{\text{PC}} = 4.5$ Hz, $^2J_{\text{PC}} = 9.3$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): I (X-ray): δ –10.11 (d, $^2J_{\text{PP}} = 16.3$ Hz); –11.60 (d, $^2J_{\text{PP}} = 16.5$ Hz); II: δ –9.66 (d, $^2J_{\text{PP}} = 16.8$ Hz); –10.14 (d, $^2J_{\text{PP}} = 17.2$ Hz). MS (EI): m/z 477 ($\text{M}^+ - \text{CO}$); 447 ($\text{M}^+ - \text{CO} - \text{NO}$); 442 ($\text{M}^+ - \text{CO} - \text{Cl}$). Anal. Found: C, 23.78; H, 4.15; N, 3.02; Re, 36.63. $\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{NO}_2\text{P}_2\text{Re}$ (505.16) Calc.: C, 23.77; H, 3.95; N, 2.77; Re, 36.86%.

2.11. Crystal structure determinations of 2, 4, 5, 6, 8, 9 and 10

The crystals were glued onto a glass fiber using epoxy resin and mounted onto the diffractometer (Mo K α $\lambda = 0.71073$ Å). Except for **4** ($T = 233$ K) the measurements were carried out at RT. The unit cell param-

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **6**

Atom	x	y	z	U_{eq}^a
Re(1)	3094(1)	1169(1)	–2198(1)	38(1)
Re(2)	8873(1)	5042(1)	–3069(1)	44(1)
C1(1)	6112(3)	4377(3)	–2986(2)	65(1)
C1(2)	8727(4)	7299(3)	–2470(2)	66(1)
C1(3)	9422(4)	4620(3)	–1482(2)	68(1)
C1(4)	3711(3)	–54(3)	–1411(2)	60(1)
N(1)	1204(9)	1190(8)	–1424(6)	43(3)
N(2)	4202(9)	2480(7)	–919(5)	42(3)
N(3)	2710(9)	2464(8)	–2797(6)	45(3)
N(4)	8531(11)	5365(10)	–4281(7)	61(4)
O(1)	1199(10)	–1038(9)	–3856(6)	83(4)
O(2)	6108(9)	1046(9)	–3049(6)	71(4)
O(3)	2485(8)	3322(9)	–3192(7)	71(4)
O(4)	8388(12)	5547(10)	–5044(6)	82(4)
O(5)	9118(9)	2220(8)	–3765(7)	77(4)
O(6)	12406(10)	6225(9)	–2914(7)	75(4)
C(1)	1917(12)	–226(11)	–3259(8)	54(4)
C(2)	5027(12)	1121(10)	–2740(7)	46(4)
C(3)	9004(11)	3286(10)	–3514(8)	46(4)
C(4)	11122(13)	5748(10)	–2970(8)	51(4)
C(10)	–276(11)	556(10)	–1738(9)	51(4)
C(11)	–1446(14)	598(12)	–1189(10)	63(5)
C(12)	–1082(14)	1345(12)	–324(9)	63(5)
C(13)	471(15)	2030(12)	18(9)	61(5)
C(14)	1595(12)	1921(10)	–538(7)	47(4)
C(15)	3262(12)	2594(10)	–268(7)	49(4)
C(16)	3870(16)	3283(11)	633(9)	65(5)
C(17)	5450(16)	3854(12)	850(8)	68(5)
C(18)	6381(15)	3789(12)	177(9)	64(5)
C(19)	5735(12)	3072(10)	–691(8)	51(4)
Cl(2S)	2676(5)	1238(5)	4721(3)	107(2)
Cl(1S)	5908(5)	2081(5)	4534(4)	130(3)
Cl(1S)	4196(15)	2578(14)	4567(12)	91(7)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for 8

Atom	x	y	z	U_{eq}^a
Re(1)	1769(1)	1565(1)	3697(1)	30(1)
P(1)	917(1)	2286(1)	4103(1)	31(1)
P(2)	–417(1)	3170(1)	3454(1)	41(1)
P(3)	2535(1)	907(1)	3008(1)	35(1)
P(4)	2929(1)	516(1)	1290(1)	43(1)
Cl(1)	2865(1)	2005(1)	2741(1)	55(1)
Cl(2)	–222(1)	1507(1)	2672(1)	44(1)
N(1)	904(4)	1236(1)	4392(2)	50(1)
O(1)	4175(4)	1613(1)	4989(2)	85(1)
O(2)	340(4)	1017(1)	4828(2)	74(1)
C(1)	3261(4)	1598(2)	4471(3)	40(1)
C(2)	234(4)	2617(1)	3213(2)	39(1)
C(10)	–478(4)	2278(1)	4699(2)	39(1)
C(11)	–1447(4)	1951(2)	4523(3)	50(1)
C(12)	–2619(5)	1960(2)	4881(3)	67(1)
C(13)	–2826(5)	2288(2)	5410(3)	69(1)
C(14)	–1881(5)	2615(2)	5599(3)	67(1)
C(15)	–707(5)	2612(2)	5245(3)	54(1)
C(3)	2280(4)	969(1)	1893(2)	39(1)
C(20)	2242(4)	2609(1)	4683(2)	36(1)
C(21)	2593(4)	2534(2)	5515(3)	53(1)
C(22)	3658(5)	2754(2)	5955(3)	63(1)
C(23)	4380(5)	3049(2)	5567(3)	73(1)
C(24)	4067(5)	3124(2)	4736(3)	69(1)
C(25)	2988(4)	2903(2)	4292(3)	52(1)
C(30)	557(4)	3541(1)	2891(3)	48(1)
C(31)	907(5)	3944(2)	3249(3)	65(1)
C(32)	1625(5)	4250(2)	2851(4)	87(1)
C(33)	1982(5)	4153(2)	2112(4)	92(1)
C(34)	1634(6)	3765(2)	1743(4)	91(1)
C(35)	941(5)	3455(2)	2131(3)	71(1)
C(40)	–2066(4)	3155(2)	2806(3)	47(1)
C(41)	–2459(5)	3437(2)	2157(3)	66(1)
C(42)	–3800(6)	3427(2)	1750(3)	90(1)
C(43)	–4702(6)	3142(2)	1989(4)	98(1)
C(44)	–4324(6)	2865(2)	2630(4)	103(1)
C(45)	–3019(5)	2873(2)	3026(4)	78(1)
C(50)	1588(4)	422(1)	3238(3)	42(1)
C(51)	532(4)	259(2)	2703(3)	53(1)
C(52)	–232(5)	–91(2)	2931(3)	70(1)
C(53)	56(5)	–273(2)	3689(3)	79(1)
C(54)	1097(5)	–118(2)	4234(3)	76(1)
C(55)	1880(5)	234(2)	4013(3)	50(1)
C(60)	4312(4)	763(2)	3248(3)	48(1)
C(61)	5252(5)	1096(2)	3276(3)	69(1)
C(62)	6595(5)	1007(2)	3360(4)	92(1)
C(63)	7049(6)	576(3)	3467(4)	107(1)
C(64)	6126(6)	244(3)	3426(4)	101(1)
C(65)	4767(5)	331(2)	3318(3)	71(1)
C(70)	4637(4)	697(2)	1165(3)	50(1)
C(71)	5077(5)	1125(2)	1163(1)	77(1)
C(72)	6381(5)	1223(2)	1033(4)	92(1)
C(73)	7246(5)	894(2)	908(4)	88(1)
C(74)	6827(5)	468(2)	917(4)	103(1)
C(75)	5537(5)	366(2)	1055(4)	84(1)
C(80)	1965(4)	655(2)	285(3)	45(1)
C(81)	2490(6)	845(2)	–344(3)	104(1)
C(82)	1682(7)	929(3)	–1087(4)	135(1)
C(83)	404(7)	825(2)	–1216(3)	101(1)
C(84)	–138(6)	643(3)	–602(4)	110(1)
C(85)	636(5)	553(2)	139(3)	87(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for **9**

Atom	x	y	z	U_{eq}^a
Re(1)	5000	0	0	35(1)
P(1)	6082(1)	1243(1)	−304(1)	41(1)
P(2)	4446(1)	552(1)	−1296(1)	41(1)
Cl(1)	5344(2)	−459(2)	−1601(3)	50(1)
N(1)	4797(9)	389(9)	1277(11)	105(1)
O(1)	4618(6)	643(6)	2059(8)	69(1)
C(1)	4746(3)	1342(3)	−1447(5)	48(1)
C(2)	7149(4)	985(4)	−1345(6)	66(1)
C(3)	7661(5)	1047(5)	−2162(7)	86(1)
C(4)	7756(5)	1504(5)	−3199(7)	93(1)
C(5)	7362(4)	1857(4)	−3307(6)	76(1)
C(6)	6830(4)	1784(3)	−2447(5)	60(1)
C(7)	6644(3)	1759(3)	992(5)	41(1)
C(8)	6332(4)	2028(3)	1768(6)	56(1)
C(9)	6688(4)	2352(3)	2835(6)	62(1)
C(10)	7376(4)	2414(3)	3084(6)	66(1)
C(11)	7698(4)	2160(4)	2283(6)	66(1)
C(12)	7333(3)	1829(4)	1208(5)	56(1)
C(13)	3540(3)	458(3)	−970(5)	49(1)
C(14)	2923(4)	57(4)	−1657(7)	69(1)
C(15)	2245(5)	−8(5)	−1350(8)	92(1)
C(16)	2196(5)	344(5)	−319(8)	98(1)
C(17)	2831(5)	766(5)	367(8)	92(1)
C(18)	3474(4)	811(4)	58(6)	69(1)
C(19)	4389(3)	364(3)	−2875(5)	47(1)
C(20)	4699(4)	936(4)	−3689(6)	69(1)
C(21)	4568(5)	746(5)	−4883(6)	93(1)
C(22)	4169(5)	27(5)	−5265(6)	86(1)
C(23)	3900(5)	−540(4)	−4442(6)	79(1)
C(24)	4002(4)	−362(3)	−3240(6)	62(1)
C(30)	5734(4)	1842(3)	−807(6)	57(1)
C(31)	5037(3)	1550(3)	−1192(5)	52(1)
F(1)	7337(3)	3411(3)	5587(5)	109(1)
F(2)	6667	3333	7234(7)	71(1)
B(1)	6667	3333	6023(9)	52(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

ters were determined and refined from a set of 24 to 36 equivalent reflections ($20^\circ < 2\theta < 28^\circ$). Data were collected through ω – 2θ scans with variable scan speeds and a scan width adapted to the peak profile. After every 97 collected reflections, three standard reflections were measured. In all cases no decay in intensity was observed. The structures were solved using the SHELXTL PLUS program package [31]. The heavy atoms were located by the Patterson method and standard Fourier techniques were used for the positioning of the remaining non-hydrogen atoms in the molecules. All hydrogen atoms were included in the calculations of the atomic positions as fixed contributors. An empirical absorption correction (DIFABS [32]) was employed. The min./max. residues found for all compounds were located in all structures in the vicinity of the rhenium atoms. Non-resolvable disorder in the CO and NO positions was found in **5** (racemate), in the anion of **6** and in **8**. As a result of this the Re–N/Re–C and N–O/C–O dis-

tances and the temperature factors of the N- and C-atoms in **5**, **6** and **8** are similar. The structure of **10A** was solved in the monoclinic space group $C2$ with the following cell parameters: $a = 14.265(3)$, $b = 9.217(2)$, $c = 26.088(5)$ Å, $\beta = 105.86(2)^\circ$. The two independent molecules in the asymmetric unit were refined with $R = 0.0302$, $wR = 0.0407$. However, inspection of the b, c -projection of the $C2$ unit cell revealed an additional symmetry relationship ($0.5 - z$) relating both RR and SS forms. Thus, the unit cell parameters were successfully checked for higher symmetry. The vectors $[-1, 0, 0]$, $[-1, 0, -2]$, $[0, -1, 0]$ define a cell with $a = 14.265(3)$, $b = 50.190(10)$, $c = 9.217(2)$ Å in the space group $Fdd2$. The refinements led to R factors $R = 0.0186$, $wR = 0.0256$. IR data for **1–10** are given in Table 1; atomic coordinates and selected bond lengths and bond angles are given in Tables 2–15. Table 16 lists details of the crystal parameters, the data collection and the structure refinement.

Table 8

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^{-3}$) for 10

Atom	x	y	z	U_{eq}^a
Re(1)	7742(1)	9598(1)	0	28(1)
P(1)	8951(3)	9301(1)	−997(2)	35(1)
P(2)	8461(1)	9487(1)	2264(2)	32(1)
C(1)	6808(1)	9200(1)	507(2)	46(1)
C(2)	7053(2)	9600(1)	−2457(3)	52(1)
O(1)	6110(4)	9930(2)	1333(9)	64(2)
O(2)	8950(5)	10072(1)	−286(8)	60(2)
N(1)	8457(4)	9884(1)	−208(7)	38(2)
C(1)	6707(5)	9812(2)	857(9)	39(2)
C(10)	9736(5)	9225(2)	523(10)	47(2)
C(11)	9170(5)	9187(2)	1910(9)	41(2)
C(12)	9900(6)	9094(2)	3018(11)	55(3)
C(13)	10560(8)	8920(2)	2095(12)	67(3)
C(14)	10371(6)	8975(2)	488(12)	61(3)
C(15)	8547(8)	8998(2)	−1821(14)	69(3)
C(16)	9695(6)	9446(2)	−2376(16)	67(3)
C(17)	9251(7)	9732(2)	2980(11)	57(3)
C(18)	7725(6)	9402(2)	3808(11)	58(3)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9

Selected bond distances (\AA) and angles ($^\circ$) for 2

Re1–Cl1	2.390(4)	Re1–Cl2	2.498(4)
Re1–N1	1.760(13)	Re1–C1	1.953(19)
Re1–C2	2.353(18)	Re1–C3	2.262(15)
Cl1–O1	1.153(22)	N1–O2	1.168(18)
C2–C3	1.397(21)		
Cl1–Re1–Cl2	86.4(1)	Cl2–Re1–Cl2A	80.8(1)
Cl2–Re1–N1	91.8(4)	Cl1–Re1–N1	178.1(4)
Cl2–Re1–C1	168.6(6)	Cl1–Re1–C1	88.5(5)
Re1–N1–O2	170.3(12)	C2–Re1–C3	35.2(5)
Re1–C1–O1	176.7(17)		

Table 10

Selected bond distances (\AA) and angles ($^\circ$) for 4

Re1–Cl1	2.412(3)	Re1–N1	2.166(8)
Re1–(C10/N)	1.888(11)	(C10/N)–O	1.138(16)
N1–C1	1.346(11)	N1–C5	1.355(12)
C3–C6	1.491(19)	C5–C5a	1.498(14)
Cl1–Re1–N1	87.8(2)	Cl1–Re1–C10	93.9(4)
N1–Re1–C10	97.0(4)	Cl1–Re1–Cl1a	170.0(2)
N1–Re1–N1A	75.1(4)	C10–Re1–N	90.8(7)

Table 11

Selected bond distances (\AA) and angles ($^\circ$) for 5

Re–Cl	2.405(4) av.	Re1–O4	2.159(9)
Re1–C1	1.952(15)	Re1–C2/N1	1.860(12) av.
Cl–O1	1.147(18)		
Cl1–Re1–Cl2	88.8(1)	O4–Re1–C1	174.5(5)
Cl2–Re1–O4	86.3(3)	Cl1–Re1–O4	84.9(2)
C2–Re1–O4	95.4(5)	O4–Re1–C1	174.5(5)

Table 12
Selected bond distances (Å) and angles (°) for 6

Cation			
Re1–C14	2.384(3)	Re1–N1	2.148(9)
Re–N2	2.142(7)	Re1–N3	1.770(9)
Re1–C1	1.982(10)	Re1–C2	1.993(11)
N3–O3	1.163(13)	C1–O1	1.143(12)
C2–O2	1.128(14)		
Cl4–Re1–N1	88.7(2)	Cl4–Re1–N2	85.1(2)
N1–Re1–N2	76.8(3)	Cl4–Re1–N3	177.7(3)
N1–Re1–C1	97.1(4)	N2–Re1–C1	171.4(4)
N1–Re1–C2	171.6(4)	N2–Re1–C2	97.1(3)
Anion			
Re2–Cl1	2.425(3)	Re2–Cl2	2.426(3)
Re2–Cl3	2.433(3)	Re2–C3	1.886(10)
Re2–C4	1.953(11)	Re2–N4	1.850(11)
C3–O5	1.148(13)	C4–O6	1.128(13)
N4–O4	1.154(14)		

Table 13
Selected bond distances (Å) and angles (°) for 8

Re1–P1	2.475(1)	Re1–P3	2.473(1)
Re1–Cl1 / 2	2.438(2) av.	Re1–N1 / C1	1.827(4) av.
P1–C2	1.832(4)	P2–C2	1.864(4)
P3–C3	1.829(4)	P4–C3	1.867(4)
P1–Re1–P3	168.4(1)	P1–Re1–Cl1	83.9(1)
P1–Re1–Cl2	88.4(1)	Cl1–Re1–Cl2	89.5(1)
P1–Re1–C1	92.4(1)	P1–Re1–C2	111.9(1)
Re1–P3–C3	111.8(1)	N1–Re1–C1	90.4(1)
P1–C2–P2	115.3(2)	P3–C3–P4	116.8(2)

Table 14
Selected bond distances (Å) and angles (°) for 9

Re1–P1	2.443(1)	Re1–P2	2.463(2)
Re1–Cl1	2.316(4)	Re1–N1	1.803(16)
P1–C1	1.820(6)	P1–C7	1.844(5)
P1–C30	1.806(9)	P2–C13	1.820(7)
P2–C19	1.821(6)	P2–C31	1.799(5)
N1–O1	1.178(21)	C30–C31	1.326(10)
B1–F1	1.331(26)	B1–F2	1.379(13)
P1–Re1–P2	79.8(1)	P1–Re1–Cl1	90.8(1)
P2–Re1–Cl1	91.8(1)	P1–Re1–N1	86.5(4)
P2–Re1–N1	90.4(6)	Cl1–Re1–N1	176.2(5)
P2–C31–C30	120.2(6)	P1–C30–C31	120.4(5)

Table 15
Selected bond distances (Å) and angles (°) for 10

Re1–P2	2.392(2)	Re1–P1	2.459(2)
Re1–Cl2	2.468(3)	Re1–Cl1	2.446(2)
Re1–N1	1.773(6)	Re1–C1	1.989(8)
N1–O2	1.178(9)	C1–O1	1.127(10)
P–C(Me)	1.795(11) av.	C–C(ring)	1.554(15) av.
P1–Re1–P2	83.3(1)	P2–Re1–Cl2	166.4(1)
P1–Re1–Cl2	86.5(1)	P2–Re1–Cl1	82.9(1)
P1–Re1–Cl1	87.6(1)	Cl1–Re1–Cl2	87.8(1)
P2–Re1–C1	95.6(2)	P1–Re1–C1	175.3(2)
Cl2–Re1–C1	93.8(2)	Cl1–Re1–N1	174.9(2)
Re1–N1–O2	177.0(6)	Cl1–Re1–C1	87.7(2)
P1–C10–C11	110.1(5)	Re1–C1–O1	178.9(6)

Table 16
Crystallographic data and processing parameters for complexes 2, 4, 5, 6, 8, 9 and 10

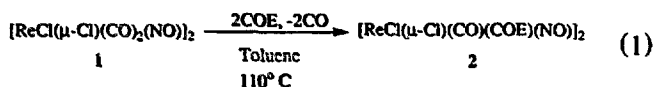
	2	4	5	6	8	9	10
Composition	$C_{12}H_{16}Cl_4N_2O_2Re_2$	$C_{11}H_{15}Cl_2N_2O_2Re \cdot CH_3CN$	$C_6H_5Cl_2NO_2Re$	$C_{13}H_{10}Cl_6N_4O_6Re_2$	$C_{51}H_{44}Cl_2NO_2P_3Re$	$C_{78}H_{66}BClF_3NOP_3Re$	$C_{10}H_{20}Cl_2NO_2P_2Re$
Crystal dimensions (mm ³)	$0.08 \times 0.04 \times 0.1$	$0.1 \times 0.4 \times 0.8$	$0.40 \times 0.20 \times 0.10$	$0.10 \times 0.07 \times 0.10$	$0.4 \times 0.3 \times 0.8$	$0.8 \times 0.7 \times 0.7$	$0.05 \times 0.05 \times 0.07$
Formula weight	567.1	541.4	415.2	927.4	1083.9	826.7	505.3
Space group	$P2_1/c$	$C2/m$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{3}$	$Fdd2$
<i>a</i> (Å)	9.47(5)	13.47(4)	6.11(3)	8.89(4)	10.02(3)	20.64(7)	14.26(3)
<i>b</i> (Å)	10.64(6)	21.71(7)	18.44(12)	10.37(2)	30.36(9)	—	50.19(10)
<i>c</i> (Å)	12.59(7)	6.49(2)	9.95(5)	14.66(4)	16.48(3)	11.32(4)	9.21(2)
α (°)	90	90	90	97.62(2)	90	90	90
β (°)	99.78(2)	105.33(2)	96.07(2)	97.46(2)	98.10(2)	90	90
γ (°)	90	90	90	102.67(2)	90	120	90
<i>V</i> (Å ³)	1251.8(12)	1831.7(9)	1116.2(10)	1290.4(6)	4971(2)	4182(3)	6599(2)
<i>Z</i>	2	4	4	2	4	4	16
ρ_{calc} (g cm ⁻³)	2.257	1.963	2.471	2.387	1.448	1.313	2.034
μ (mm ⁻¹)	10.114	6.939	11.353	10.031	2.720	2.384	7.877
2 θ range (°)	4–52	4–56	4–50	4–52	4–52	4–54	4–52
Scan speed (° min ⁻¹)	variable 1.50–14.65	variable 2.02–14.65	variable 2.02–14.65	variable 1.50–14.65	variable 2.02–14.65	variable 1.83–14.65	variable 2.02–14.65
No. of unique data	2468	2288	1953	6241	8865	6132	1638
No. of observed data	1231 ^b	2070 ^b	1340 ^a	3685 ^b	6944 ^b	4236 ^a	1463 ^b
No. of parameters refined	136	114	127	298	550	313	162
<i>R</i> (%) ^c	3.70	6.36	3.40	3.62	2.79	4.19	1.86
<i>wR</i> (%) ^d	4.54	8.83	3.87	4.11	3.03	6.93	2.56
Goodness-of-fit	0.83	1.44	3.05	0.77	1.46	0.42	0.35
Weighting scheme (1/ <i>n</i>)	$\sigma^2(F) + 0.0019F^2$	$\sigma^2(F) + 0.0030F^2$	$\sigma^2(F) + 0.0000F^2$	$\sigma^2(F) + 0.0012F^2$	$\sigma^2(F) + 0.0001F^2$	$\sigma^2(F) + 0.0269F^2$	$\sigma^2(F) + 0.0049F^2$
Max./min. residual	1.38/–1.01	4.77/–2.75	1.21/–1.31	1.50/–1.40	0.49/–0.79	3.38/–0.45	0.63/–0.54
electron density (e Å ⁻³)							

^a With $|F_o| \geq 6\sigma(|F_o|)$. ^b With $|F_o| \geq 4\sigma(|F_o|)$. ^c $\Sigma||F_o| - F_c|/\Sigma F_o$. ^d $[\Sigma w(|F_o| - F_c)|^2]/\Sigma w|F_o|^2)^{1/2}$.

3. Results and discussion

3.1. Crystal structure of $[\text{ReCl}(\mu\text{-Cl})(\text{CO})(\text{COE})(\text{NO})]_2$ (**2**)

Complex **2** was synthesized with minor changes following the original report [20] (Eq. (1)).



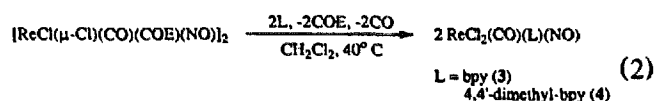
Suitable needles for an X-ray analysis were obtained from a dichloromethane/pentane solution. The unit cell of **2** contains two binuclear rhenium complexes. In these dimers (Fig. 1) the octahedrally coordinated Re atoms are connected by chlorine bridges with an inversion center in the middle of the planar $\{\text{Re}(\mu\text{-Cl})_2\text{Re}\}$ arrangement ($\text{Re1}-\text{Cl2}$ 2.498(4) Å).

2 contains chiral Re centers and represents a *meso* form. One CO group ($\text{Re1}-\text{C1}$ 1.953(19) Å) and the π bonded COE ligand are *trans* to the bridging chlorine atoms. Differences in the $\text{Re}-\text{C2}$ (2.353(18) Å) and $\text{Re}-\text{C3}$ (2.262(15) Å) distances reveal a certain degree of asymmetry in the COE binding. This is presumably due to steric interactions. Too large standard deviations prevent the observation of any particular elongation of the coordinated C=C double bond ($\text{C2}-\text{C3}$ 1.397(21) Å). The NO ligand ($\text{Re1}-\text{N1}$ 1.760(13) Å, $\text{N1}-\text{O2}$ 1.168(18) Å) occupies one axial position *trans* to the terminal chlorine atom ($\text{Re1}-\text{Cl1}$ 2.390(4) Å). The $\text{Re}-\text{N1}-\text{O2}$ angle ($170.3(12)^\circ$) deviates from linearity. There is however no obvious reason for this. In **2** the $\text{Re}-\text{Cl}_{\text{term}}$ bond is particularly short in comparison with such of P donor substituted compounds like *cis,trans*- $[\text{ReCl}_2(\text{PEt}_3)_2(\text{CO})(\text{NO})]$ [12] ($\text{Re}-\text{Cl}$ 2.440(2) Å av.), but it is similar to that found in $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ (2.405(9) Å av.) (vide infra) and 0.1 Å shorter than the bridging $\text{Re}-\text{Cl2}$ distance. Finally it should be noted that the planar $\{\text{Re}(\mu\text{-Cl})_2\text{Re}\}$ frag-

ment in **2** is practically isostructural with that in $[\text{Re}(\mu\text{-Cl})(\text{THF})(\text{CO})_3]_2$ ($\text{Re}-\text{Cl}_{\text{br}}$ 2.505(6) Å and $\text{Cl}-\text{Re}-\text{ClA}$ $81.3(2)^\circ$) [33]. Selected bond distances and angles for **2** are given in Table 9.

3.2. Synthesis of $\text{ReCl}_2(\text{L})(\text{CO})(\text{NO})$ ($\text{L} = \text{bpy}$ (**3**), 4,4'-dimethyl-bpy (**4**))

Reaction of **2** with an equimolar amount of 2,2'-bipyridine in boiling dichloromethane results in the formation of **3** (Eq. (2)) which precipitates as a dark red powder.



The insolubility of **3** in almost all solvents (with the exception of dimethylformamide) renders its spectroscopic characterization rather difficult. Crystallization attempts from a dimethylformamide mixture yielded after a few months rubin-like crystals, which were analyzed by X-ray diffraction. They showed good diffraction properties, but a complex positional disorder of the ligand sphere caused by the high symmetry of the $\text{C2}/m$ space group (Re atom in a special position) prevented an acceptable structure solution with the collected data. Nevertheless, the presence of the $\{\text{Re}(\text{bpy})(\text{CO})(\text{NO})\}$ fragment in **3** was indicated by the position of the $\nu(\text{CO})$ and $\nu(\text{NO})$ IR absorptions ($\nu(\text{CO})$ 1967 cm^{-1} , $\nu(\text{NO})$ 1725 cm^{-1}) and of $\nu(\text{CH})$ and $\nu(\text{CC})$ vibrations of the bipyridine ligand. To obtain more information about the structure of **3** we attempted the synthesis of a related complex with the more soluble 4,4'-dimethyl-2,2'-bipyridine.

Under similar reaction conditions as for **3**, **4** was prepared in 55% yield (Eq. (2)). This compound was soluble in polar solvents, allowing its spectroscopic characterization in solution. The ^1H NMR spectrum of **4**

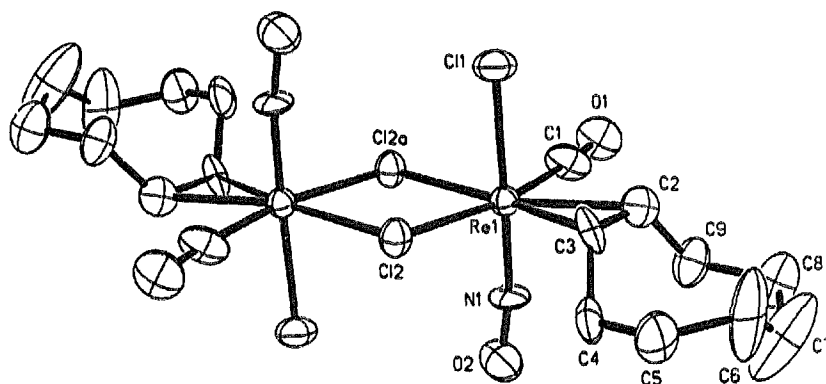


Fig. 1. Molecular structure of $[\text{ReCl}(\mu\text{-Cl})(\text{CO})(\text{COE})(\text{NO})]_2$ (**2**). Ellipsoids are drawn with 40% probability.

displays two singlet signals at 2.65 and 2.75 ppm for the methyl substituents and the ^{13}C NMR spectrum shows non-equivalent signals for the two pyridyl units (methyl substituents at 21.38 and 21.83 ppm). A singlet signal at 214.8 ppm was assigned to the carbonyl group. IR bands for the coordinated CO, NO groups ($\nu(\text{CO})$ 1973 cm^{-1} , $\nu(\text{NO})$ 1718 cm^{-1}) and FAB-MS peaks at 499, 471 ($-\text{CO}$), 464 ($-\text{Cl}$) also supported the given structural assignment. Finally an X-ray diffraction study was carried out on **4**. In consideration of the earlier reported observations [27] on the reactivity of **1**, we presume that the first step in the reaction of **2** with a Lewis base involves splitting of the chlorine bridges giving $[\text{ReCl}_2(\text{CO})(\text{COE})(\text{NO})\text{L}]$ mononuclear species. It is suggested that for $\text{L} = \text{bpy}$ the fission of the Cl bridges occurs with regiospecificity in such a way that a *trans* η^1 -bpy, CO intermediate is formed. Subsequent replacement of the Cl ligand *trans* to the NO group by the second pyridyl residue produces an ionic $[\text{ReCl}(\eta^2\text{-bpy})(\text{CO})(\text{COE})(\text{NO})]\text{Cl}$ complex, which can undergo COE substitution by the free chloride. It should be noted at this point that the reaction of $\text{Re}(\text{CO})_2(\text{NO})\text{Cl}_2(\text{THF})$ with bpy (vide infra) leads to a different cationic product with exchange of one Cl and one CO group.

3.3. Crystal structure of $\text{ReCl}_2(4,4'\text{-dimethyl-bpy})(\text{CO})(\text{NO})$ (**4**)

The rhenium center in **4** (Fig. 2) is pseudo-octahedrally coordinated with two almost linearly disposed chlorine atoms ($\text{Re}=\text{Cl1}$ 2.412(3) Å, $\text{Cl1}-\text{Re1}-\text{Cl1a}$ 170.0(2)°). The CO, NO groups are disordered and are copolar with the bipyridine unit. The $\text{Re}=\text{Cl1}$ distance is about 0.080(2) Å shorter than that in $(\eta^2\text{-tpy})\text{Re}(\text{CO})_2\text{Cl}$ (2.493(1) Å) [34], presumably reflecting the enhanced hardness of the metal center in **4**. Selected bond distances and angles are given in Table 10.

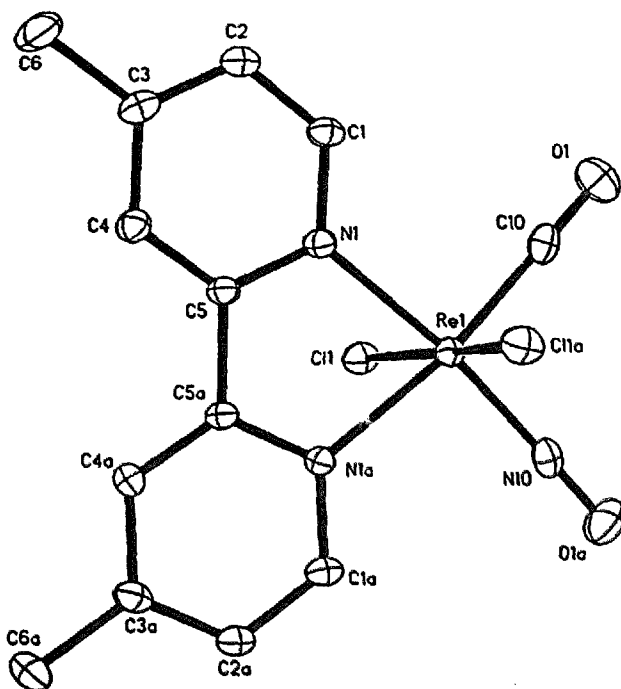
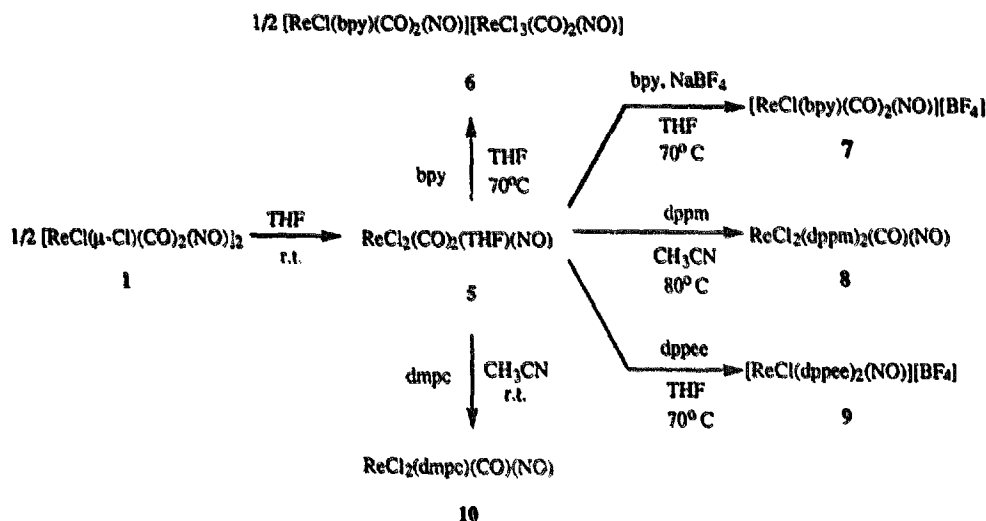


Fig. 2. Molecular structure of $\text{ReCl}_2(4,4'\text{-dimethyl-bpy})(\text{CO})(\text{NO})$ (**4**). Ellipsoids are drawn with 30% probability.

3.4. Synthesis and crystal structure of $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ (**5**)

Dissolution of **1** in THF results in a quantitative formation of **5** within 20 min at RT (Scheme 1). After this time the $\nu(\text{CO})$, $\nu(\text{NO})$ bands of **1** could no longer be detected by IR monitoring. $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ (**5**) was isolated in 95% yield. The mononuclear nature of **5** has been assured by FAB-MS measurements (M^+ peak at 415, $M^+ - \text{CO}$ at 387). The coordination of the THF molecule was confirmed by resonances for the methylene groups of the THF moiety in the ^1H (multiplets at 0.96 and 3.70 ppm) and ^{13}C NMR spectrum



Scheme 1.

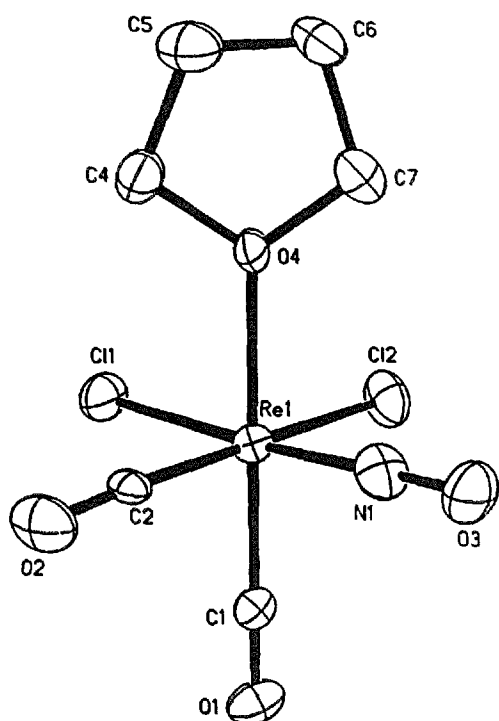


Fig. 3. Molecular structure of $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ (**5**). Ellipsoids are drawn with 30% probability.

(singlets at 25.5 and 76.0 ppm). Furthermore, in the ^{13}C NMR spectrum the inequivalence of the carbonyl groups leads to two singlet signals in the expected chemical shift region (185.4 and 186.7 ppm with 2:1 intensity). In the IR spectrum of **5** the $\nu(\text{CO})$ and $\nu(\text{NO})$ absorptions are shifted to lower wavelengths with respect to **1** (see Table 1), indicative of a stronger π backbonding. If the splitting of the bridges of **1** by THF occurs with retention of the configuration at the Re centers, the formation of a racemic mixture of **5** is predicted. This indeed can be observed in the solid state structure.

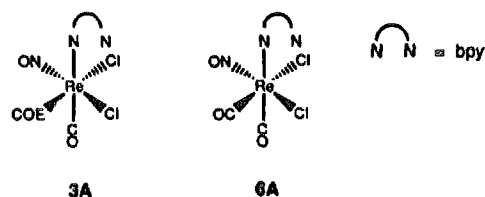
The pseudo-octahedral Re center in **5** bears one THF group ($\text{Re}-\text{O}4$ 2.159(9) Å) and one CO ligand ($\text{Re}-\text{C}1$ 1.952(15) Å, $\text{C}1-\text{O}1$ 1.478(18) Å) *trans* to each other (Fig. 3). The *cis* CO, NO groups are positionally disordered and lie in one plane with the two Cl atoms ($\text{Re}-\text{Cl}$ 2.405(4) Å). Selected bond distances and angles of **5** are compiled in Table 11. The $\text{Re}-\text{O}4$ bond is slightly shorter than that in $[\text{Re}(\text{THF})(\mu\text{-Cl})(\text{CO})_3]_2$ (2.213(10) Å) [33] and the $\text{Re}-\text{Cl}$ average distances are significantly shorter than in $\text{Re}(\text{CO})_5\text{Cl}$ (2.515(2) Å, about 0.1 Å) [35].

3.5. The reaction of $\text{ReCl}_2(\text{CO})_2(\text{THF})(\text{NO})$ (**5**) with 2,2'-bipyridine

5 was reacted with 2,2'-bipyridine in boiling THF. After about 10 h an orange–yellow precipitate of **6** was formed and after about two days the starting material was completely consumed (IR monitoring). During this

time no additional bands for an intermediate species could be detected. **6** is soluble in acetone and acetonitrile, but practically insoluble in all other solvents. The IR spectrum (2200–1700 cm^{-1} , see Table 1) was quite complicated, because the CO and NO groups displayed four and two bands respectively. Likewise in the ^{13}C NMR spectrum two signals were observed for the CO groups at 186.7 and 188.8 ppm and five singlet signals in the aromatic region for the equivalent pyridyl units of the bpy substituent. In the ^1H NMR spectrum a resonance pattern appeared, which was similar to that of uncoordinated 2,2'-bipyridine, but shifted about 0.7 ppm to lower fields. These observations were consistent with the ionic nature of **6** containing two types of Re center (Scheme 1).

Thus, the bpy substitutions of **2** and **5** took quite different courses, even though the inner coordination spheres of both complexes appear to be quite similar. The formation of different products **3** and **6** can presumably be related to the intermediacy of the species **3A** and **6A**, which differ by the replacement of a COE with a CO ligand.



Apparently in **3A** the Cl *trans* to NO is more labile and is substituted by a 'free leg' of bpy, while in **6A** the more activated chloride position *trans* to CO is exchanged. The free chloride of **3A** can subsequently replace the COE moiety, thus creating a *trans* Cl_2 arrangement.

The structure of **6** was finally manifested by an X-ray diffraction study (Fig. 4). Selected bond distances and angles for **6** are reported in Table 12. The anion of **6** possesses an octahedrally coordinated Re center ($\text{Re}2$) with three facially coordinated chlorine atoms. Because of the similarity of the $\text{Re}2-\text{N}4$, $\text{Re}2-\text{C}3$ (1.850(11) vs. 1.886(10) Å) and $\text{N}4-\text{O}4$, $\text{C}3-\text{O}5$ (1.154(14) vs. 1.148(13) Å) bond distances, we believe that the positions of the N4, C3 atoms are disordered to some extent. The structural features of this anion are very similar to that of *fac*- $[\text{PPN}][\text{ReCl}_3(\text{CO})_2(\text{NO})]$ [36]. The cation of **6** contains the Re1 atom in a slightly distorted octahedral environment, one chlorine atom ($\text{Re}1-\text{Cl}4$ 2.384(3) Å) and one nitrosyl ligand ($\text{Re}1-\text{N}3$ 1.770(9) Å and $\text{N}3-\text{O}3$ 1.163(13) Å) are *trans* to each other, while the 2,2'-bipyridine moiety ($\text{Re}1-\text{N}$ 2.145(7) Å av.) is located *trans* to two carbonyl ligands ($\text{Re}1-\text{C}$

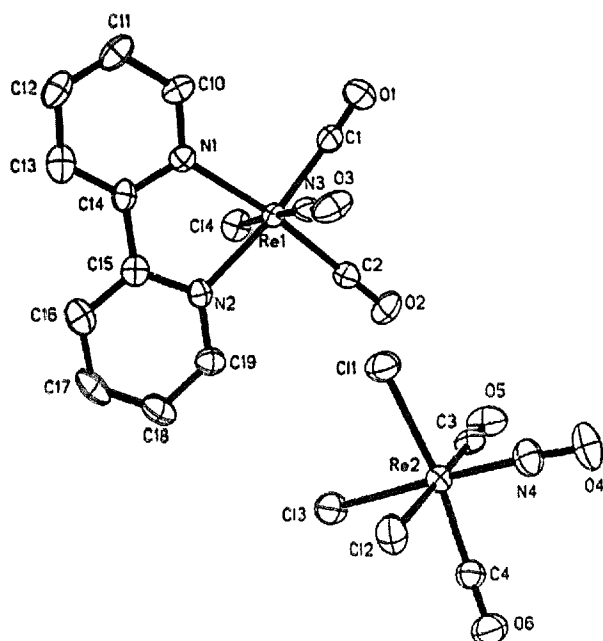


Fig. 4. Molecular structure of $[\text{ReCl}(\text{CO})_2(\text{bpy})(\text{NO})]$ ($[\text{ReCl}_2(\text{CO})_2(\text{NO})]$ (**6**). Ellipsoids are drawn with 30% probability.

1.989(10) Å av., C–O 1.130(13) Å). The Re1–Cl4 distance in the cation is about 0.04 Å shorter than the average Re–Cl bond found in the anion and about 0.10 Å shorter than the analogous bond in $\text{ReCl}(\text{CO})_3(\sigma^2\text{-tpy})$ (2.493(1) Å) [34]. In the formation of **6** the replaced chloride substituent of **6A** is accepted by a molecule of **5** yielding the $[\text{ReCl}_2(\text{CO})_2(\text{NO})]^-$ anion. In principle, this acceptor function could be taken over by, for instance, Na^+ sources like NaBF_4 leading to the precipitation of NaCl . The BF_4^- would remain as a counterion for the organometallic cation, which could be of great advantage, since BF_4^- generally enhances solubilities of salts in less polar solvents.

Under the same conditions as for the preparation of **6** the reaction of **5** with NaBF_4 and 2,2'-bipyridine led to a yellow–orange precipitate, which was characterized as **7**. The CO and NO substituents of **7** showed the same IR absorption bands as those assigned for the cation in **6**. The presence of a non-coordinated BF_4^- anion was assured by the appearance of one strong band at 1070 cm^{-1} (in the solid state), which displayed a typical splitting of the B–F stretching vibration [37] in the range $1109\text{--}1024\text{ cm}^{-1}$, and in addition by a signal in the ^{19}F NMR spectrum at -152 ppm .

3.6. Substitution reactions of **5** with ligands of the type $\text{PPh}_2\text{--}(\text{CH}_2)_n\text{--PPh}_2$ ($n = 1, 2$)

It was shown [20,27,28] that compounds of the type $\text{cis,trans-}[\text{ReCl}_2\text{L}_2(\text{CO})(\text{NO})]$ (L = monodentate P donors) can be prepared by the reaction of $[\text{ReCl}(\mu\text{-Cl})(\text{CO})_2(\text{NO})]_2$ in coordinating solvents (like THF or

CH_3CN) or of $[\text{ReCl}(\mu\text{-Cl})(\text{COE})(\text{CO})(\text{NO})]_2$ in toluene with 4 equivalents of L.

Therefore **5** was reacted with 1,2-bis(diphenylphosphine)ethane (dppe) in CH_3CN . After a few hours a precipitate was formed, but the insolubility of this compound in all solvents made its full characterization impossible. Nevertheless its solid state IR spectrum indicated the presence of the coordinated phosphine ligand ($\nu(\text{C--H}_{\text{ph}})$ at $3050\text{--}3070\text{ cm}^{-1}$, $\nu(\text{C--H}_{\text{aliph}})$ at $2940\text{--}2990\text{ cm}^{-1}$ and $\nu(\text{C=C}_{\text{ph}})$ at $1413, 1436$ and 1485 cm^{-1}), one carbonyl ($\nu(\text{CO})$ 2000 cm^{-1}) and one nitrosyl substituent ($\nu(\text{NO})$ 1732 cm^{-1}). If a polymeric structure were the reason for the poor solubility, then the use of the more rigid 1,2-bis(diphenylphosphine)methane (dppm) should sterically prevent the formation of polynuclear species. In fact, the reaction of **5** with dppm in acetonitrile led within 14 h to the formation of a yellow product **8** with high solubility in polar as well as chlorinated solvents (Scheme 1). Gas evolution was observed during the reaction and IR detection indicated the disappearance of one CO band. The positions of the $\nu(\text{CO})$, $\nu(\text{NO})$ absorptions of **8** are practically identical to those of the previously reported $\text{ReCl}_2(\text{PPh}_3)_2(\text{CO})(\text{NO})$ species [13,20] ($\nu(\text{CO})$ 2007 cm^{-1} , $\nu(\text{NO})$ 1738 cm^{-1}) displaying *trans* P donors. The ^{13}C NMR spectrum of **8** confirmed the presence of one CO group (broad signal at 197.8 ppm) and the ^{31}P NMR spectrum showed virtual triplets for the two non-equivalent P nuclei at 1.70 and -28.5 ppm . The observation of virtual triplet resonances was also reported for the similar *fac*- $[\text{Re}(\text{CO})_3\text{Br}(\mu\text{-}(\text{Me}_2\text{PCH}_2\text{PMe}_2)_2)]$ compound [38]. By cooling a dichloromethane/pentane mixture of **8** to -20°C , yellow prisms were obtained. A crystal structure analysis confirmed the monodentate *trans*-coordination of two dppm substituents (Fig. 5).

The structure of **8** with *cis* arranged CO, NO groups (disordered) *trans* to two chlorine atoms is thus comparable with that of the *cis,trans*- $[\text{ReCl}_2(\text{PEt}_3)_2(\text{CO})(\text{NO})]$ complex [12]. The axial P–Re–P angle of **8** is comparably close ($168.4(1)^\circ$ vs. $176.8(1)^\circ$ for $[\text{ReCl}_2(\text{PEt}_3)_2(\text{CO})(\text{NO})]$). Table 13 reports selected bond distances and angles for **8**. Apparently *cis* chelation of the ppm ligand in **8** is less favorable than the coordination of two ligands in *trans* position. The use of a more rigid ligand could perhaps enforce chelation. The closest analogue of dppe with a rigid structure is 1,2-bis(diphenylphosphino)ethene [39,40] (dppee). The substitution behavior of which was therefore investigated.

3.7. Substitution reaction in **5** with 1,2-bis(diphenylphosphino)ethene (dppee)

The synthetic approaches to dppe and dppee complexes are expected to be very similar. However, **5** did

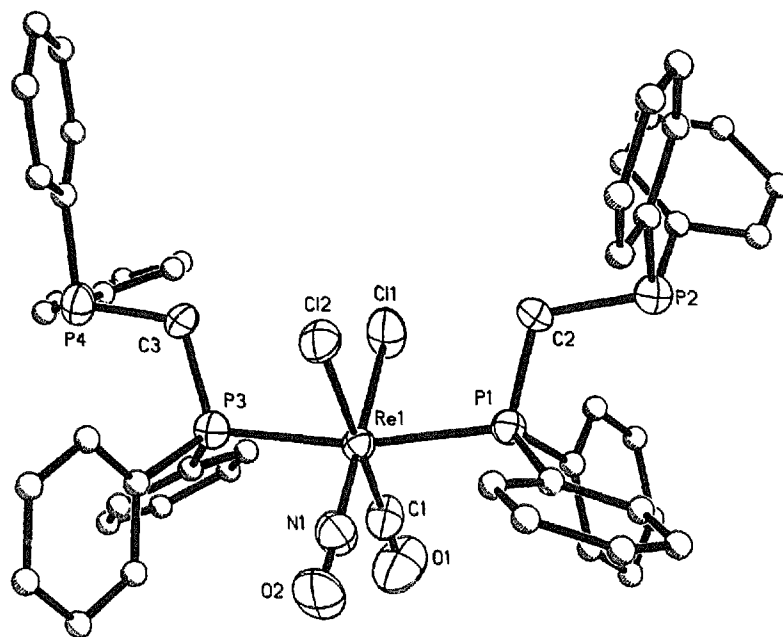


Fig. 5. Molecular structure of $\text{ReCl}_2(\text{dppe})_2(\text{CO})(\text{NO})$ (**8**). Ellipsoids are drawn with 30% probability.

not react with dppe under the same or even more forcing conditions than for the dppe ligand. Therefore **5** was then reacted with dppe in boiling THF in the presence of NaBF_4 comparable with the synthesis of **7** (Scheme 1). After two days no starting material could be detected anymore and a yellow precipitate was formed from which **9** was extracted with acetonitrile from the coprecipitated NaCl . The IR spectrum of **9** showed a strong band at 1714 cm^{-1} , which revealed the coordination of one nitrosyl group, while no absorption bands were present in the $\nu(\text{CO})$ region ($2200\text{--}1800\text{ cm}^{-1}$). Further structural information could be obtained from the ^1H and ^{31}P NMR spectra of **9**. Because of its limited solubility the complex signal patterns displayed in the ^{13}C NMR spectrum could not be assigned unambiguously. The eight phenyl residues of the ligands showed two groups of ^1H NMR signals, attributed to the rings above and below the plane containing the P atoms. The vinyl protons appear as a multiplet at about 8 ppm, while the signals at 7.42–7.50 ppm (H_{para}) and 7.22–7.36 ppm (H_{meta}) as two overlapping triplets. Moreover, a multiplet signal at 6.92–7.06 ppm is assigned to the phenyl *ortho* protons. The P atoms in **9** are chemically equivalent and display a singlet at 30 ppm in the ^{31}P NMR spectrum with a shift of 6 ppm to lower field with respect to the free molecule [41]. **9** has good solubility in hot acetonitrile and crystallizes at room temperature from this solution to yield large yellow prisms.

One of these crystals was investigated by an X-ray diffraction study. The asymmetric unit of the trigonal cell (space group $P\bar{3}$) consists of two distinct ions: a cationic rhenium moiety (Fig. 6) and a BF_4^- counterion.

Re1 occupies a special crystallographic position ($x = 0.5$, $y = 0$, $z = 0$), and therefore the P ligands are symmetry related and the Cl and the NO group are disordered. The Re center is octahedrally coordinated with practically linear arrangement of the chloride and the nitrosyl group ($176.2(5)^\circ$) and with the two dppe ligands in one plane. **9** is isostructural with the previously reported [24] $[\text{ReCl}(\text{NO})(\text{dppe})_2]^+$ dication. The Re–Cl bond in this Re(II) compound is longer than in **9** ($2.388(5)$ vs. $2.316(4)$ Å in **6**) and the Re–N distance is

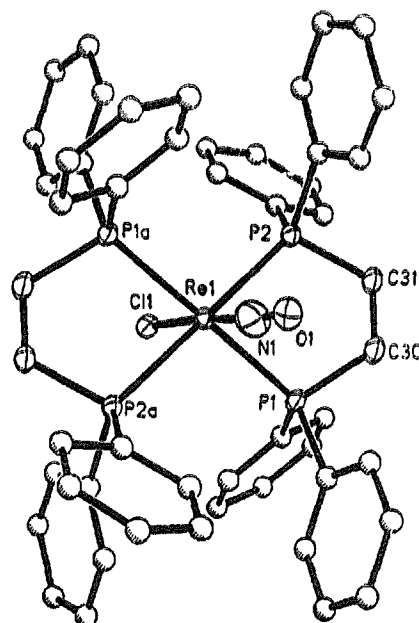


Fig. 6. Molecular structure of $[\text{ReCl}(\text{dppe})_2(\text{NO})][\text{BF}_4]$ (**9**). Ellipsoids are drawn with 30% probability.

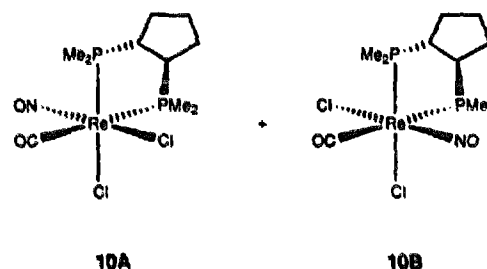
shorter (1.730(13) vs. 1.803(16) Å in **9**) concomitant with a longer N–O (1.24(2) vs. 1.178(21) Å in **9**). The position of the $\nu(\text{NO})$ bands in the IR spectrum of **9** (1714 vs. 1680 cm^{-1}) supports these structural observations. The Re1–Cl1 distance in **9** is 0.1 Å shorter than in *trans*-[Re(II)Cl₂(dppee)₂] (2.422(2) Å) [42], and practically identical to that found in *trans*-[Re(III)Cl₂(dmpe)₂][PF₆] (2.337(1) Å) [43]. The Re–P bond distances are on average 0.05 Å longer than in *trans*-[ReCl₂(dppe)₂] (2.405(2) Å av.) [42], while the P1–Re1–P2 angle of **9** is comparable with that compound (78.75(7)°). The C=C, P–C bond lengths are in the expected range and do not indicate any electron delocalization from the C=C double bond into the P–C bond [43,44]. The most important bond distances and angles of **9** are given in Table 14.

3.8. Substitution reaction in **5** with (\pm)-*trans*-1,2-bis(dimethylphosphino)cyclopentane

The use of a bidentate ligand with either high flexibility, like 1,2-bis(dimethylphosphino)ethane (dmpe), or a certain rigidity with a large bite angle should permit the stabilization of the desired [ReCl₂(CO)₂(η^1 -PP(XNO))] (PP = bidentate P donor) system. Attempts at the substitution of **5** with dmpe in acetonitrile at RT were not successful. After a few hours, IR detection of the reaction mixture indicated the presence of many products, which could not be separated. Therefore *trans*-1,2-bis(diphenylphosphino)cyclopentane (dppe) with a large bite angle, and in addition a rigid backbone, was applied. The crystal structure of the non-coordinated phosphorus derivative showed a very large P=C=C–P torsion angle (161.8°) and long PP distance (4.450 Å) [29]. Upon coordination with an (NiBr)₂ frag-

ment the torsion angle became 53.7° and the PP distance 3.021 Å, thus providing an ideal geometry for a stable chelate [29,45].

5 was reacted with a slight excess of racemic dmpe in acetonitrile at RT (Scheme 1). During the reaction the color changed from yellow to dark orange and gas evolution was observed. This was confirmed by the disappearance of one carbonyl band in the IR spectrum. After 20 h no more starting compound was detected in the reaction mixture and two broad bands evolved at 2019 and 1718 cm^{-1} . Repeated crystallizations gave orange **10** in analytically pure form. The analogous reaction in THF led to significant decomposition and therefore lower yields of **10**. The IR analysis of **10** in the solid state indicated the presence of two diastereomers **10A** and **10B**. In the ³¹P NMR spectrum they displayed two doublets (at –9.70 and –11.87 ppm) with very similar coupling constants. In the mass spectra (EI) a strong peak at 477 a.u. confirmed the presence of an {ReCl₂(NO)(dmpe)} fragment.



The two diastereomers **10A** and **10B** could not be separated by crystallization, but by careful analysis of

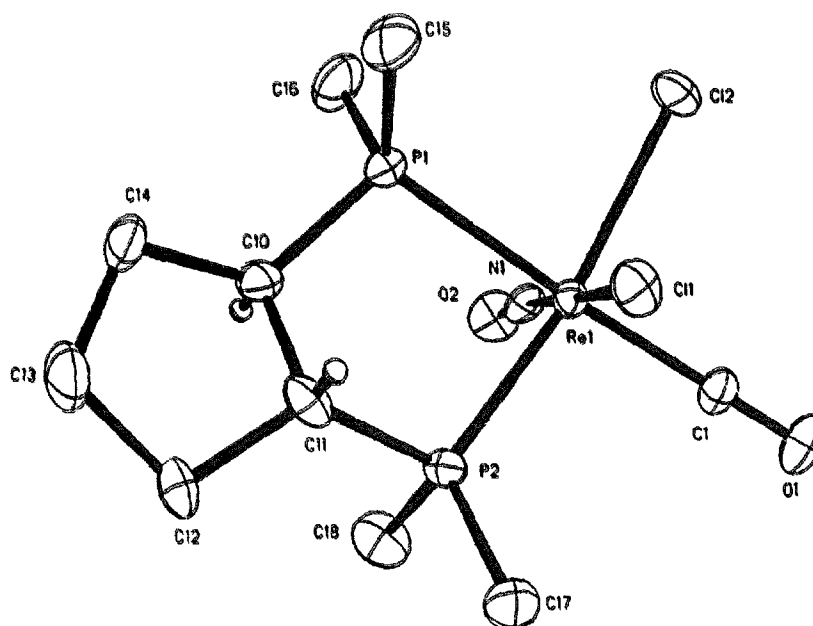


Fig. 7. Molecular structure of ReCl₂(dmpe)(CO)(NO) (**10**). Ellipsoids are drawn with 40% probability.

the crystal shapes it was possible to isolate a small amount of one diastereomer **10A** and thus to assign the ^{31}P NMR and the IR data of both diastereomers.

The structure of the enantiomeric pair of **10A** was determined by an X-ray diffraction study. The unit cell of **10A** (space group *Fdd2*) contains the two enantiomers **10A^{SS}** and **10A^{RR}**. In Fig. 7 only the **10A^{RR}** isomer is shown. Selected distances and angles are reported in Table 15. The Re center is octahedrally coordinated with one chlorine atom (Re1–Cl1 2.446(2) Å) *trans* to one nitrosyl ligand (Re1–N1 1.773(6) Å, N1–O2 1.178(9) Å). The bidentate ligand (Re1–P1 2.459(2) Å, Re1–P2 2.392(2) Å) is located *trans* to a carbonyl ligand (Re1–C1 1.989(8) Å, C1–O1 1.127(10) Å and P1–Re1–C1 175.3(2)°) and to a chlorine atom (Re1–Cl2 2.468(3) Å and P2–Re1–Cl2 166.4(1)°). The bite angle of the diphosphine in **10A** (P1–Re1–P2 83.3(1)°) is about 5° closer than in NiBr₂(dppc) [45] (88.3(3)°). The Re–Cl bond *trans* to NO (Re1–Cl1) is slightly shorter than that *trans* to P2 (Re1–Cl2), reflecting the larger *trans* influence of P2 with respect to the NO ligand. In contrast, the Re–P bond length *trans* to the chlorine atom (Re1–P2) is about 0.07 Å shorter than that *trans* to the carbonyl ligand (Re1–P1), indicating a larger *trans* influence of CO with respect to the chlorine atom in **10A**.

4. Supplementary material available

Further details of the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Requests should contain the deposition number CSD-58827, the names of authors and the journal citation.

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