

Synthesis, Characterization and Redox Behaviour of Mono- and Dicarbonyl Phosphane Rhenium(I) Complexes Bearing N-, N,N- and N,O-Type Ligands

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New mono- and dicarbonyl phosphane Re^I complexes [ReCl(L)₂(CO)(PPh₃)₂] {L = 3,5-Me₂-Hpz (**3**), quin (**4**)} and [Re(L)_n(CO)₂(PPh₃)₂][BPh₄]_m {L = pz/Hpz, *n* = 2, *m* = 0 (**2**); L = 4,7-Ph₂-phen, *n* = 1, *m* = 1 (**5**); L = 2-Me-dipic, *n* = 1, *m* = 0 (**6**)} were prepared by reaction of the dinitrogen Re^I precursor [ReCl(N₂)(CO)₂(PPh₃)₂] (**1**), in refluxing methanol or methanol/benzene mixture, with 3,5-dimethylpyrazole (3,5-Me₂-Hpz), quinoline (quin), pyrazole (Hpz), 4,7-diphenyl-1,10-phenanthroline (4,7-Ph₂-phen) and dipicolinic acid (H₂dipic), respectively, with esterification of the latter in **6** to afford the 2-methoxycarbonyl-6-pyridinecarboxylate (2-Me-dipic) moiety. Complexes **2–6** were characterized by IR spectroscopy,

¹H-, ³¹P{¹H}- and ¹³C{¹H} NMR spectroscopy, FAB-MS, cyclic voltammetry, elemental analyses and single-crystal X-ray diffraction (for **2**, **5** and **6**) analyses which indicate mutually *trans* triphenylphosphane ligands. The redox behaviour of the obtained complexes in solution was studied, and the Le-Ver electrochemical ligand parameter *E*_L was determined, for the first time, for 4,7-Ph₂-phen. Compounds **2–6** represent the first examples of *mono-* and *dicarbonyl* Re complexes bearing these types of ligands.

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Introduction

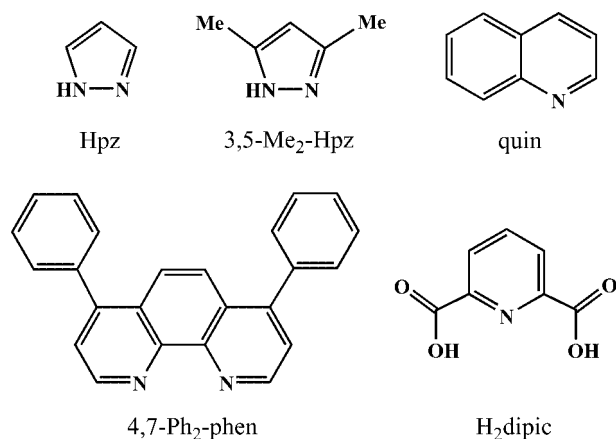
Dinitrogen complexes of rhenium are an important class of compounds within the low-oxidation-state coordination chemistry of this metal, particularly because of their significance in the field of nitrogen fixation and as versatile synthons for a variety of new rhenium derivatives.^[1,2] The lability of the coordinated N₂ in Re complexes allows its displacement by a variety of small molecules (e.g., CO, H₂, CS₂, NO, nitriles, oximes, alkynes, azides, cyanates, etc.) and various P-, N-, O-, S- or mixed-donor ligands.^[1,3] In this respect, the bis(diphosphane) complex *trans*-[ReCl(N₂)(dppe)₂] {dppe = 1,2-bis(diphenylphosphanyl)ethane} is the most studied member within the whole family of Re dinitrogen complexes.^[1b,1e,1g,3a,3e,4] A few studies have been performed on the monophosphane analogues [ReCl(N₂)(L)₄] (L = PMe₂Ph or PMePh₂),^[1b,5a,5b] whereas the reactivity of the related mixed N₂/CO complex [ReCl(N₂)(CO)₂(PPh₃)₂] (**1**) appears to have been investi-

gated only in a couple of cases; one instance involved its reactions with some amino acids conjugated with 2-aminothiazole (L) to afford monocarbonyl Re^{II} complexes of the general formula [ReCl(L)(CO)(PPh₃)₂].^[5c] The other case led to the Re^I dinitrogen compound [Re(pic)(N₂)(CO)(PPh₃)₂] (pic = picolinate) by reaction of **1** with picolinic acid (Hpic),^[6a] thus initially extending to the low Re^I oxidation state (and to picolinate) our interest in higher-oxidation-state rhenium complexes with N- or O-ligands, namely some benzoildiazenido-Re^{III}^[6b] and oxo-Re^V^[6c] compounds which were shown to act as catalysts for the peroxidative oxidation^[6b] or carboxylation^[6c] of alkanes. To further explore the use of **1** as a convenient precursor for the synthesis of new Re^I compounds with N-, N,N- or N,O-ligands, we studied its reactions with various N-heterocycle species, that is, pyrazole, 3,5-dimethylpyrazole, quinoline, 4,7-diphenyl-1,10-phenanthroline and dipicolinic acid (Scheme 1), and we prepared and characterized a series of derived mono- and dicarbonyl complexes. Although heterocycle ligands of such types are rather simple and commonly used in coordination chemistry, their complexes with the monocarbonyl {Re(CO)} or dicarbonyl {Re(CO)₂} core are still very rare.^[7] This contrasts with the tricarbonyl {Re(CO)₃} core, whose coordination chemistry was extensively developed over the last two decades,^[8] with application in nuclear-medical research, in the preparation of photoluminescent materials, in catalysis and in supramolecular chemistry.^[7a,9]

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Scheme 1.

In particular, despite the fact that a number of *tricarbonyl* Re complexes with these ligands were already known,^[10] to the best of our knowledge, there were no examples of *mono-* and *dicarbonyl* Re complexes comprising pyrazole, 3,5-dimethylpyrazole or quinoline ligands, as well as any phenanthroline or dipicolinate derivatives. The redox properties of the synthesized complexes were also investigated by cyclic voltammetry, and the value of the electrochemical Lever ligand parameter $E_L^{[11]}$ was estimated, for the first time, for the 4,7-Ph₂-phen ligand.

Results and Discussion

Synthesis and Spectroscopic Characterization

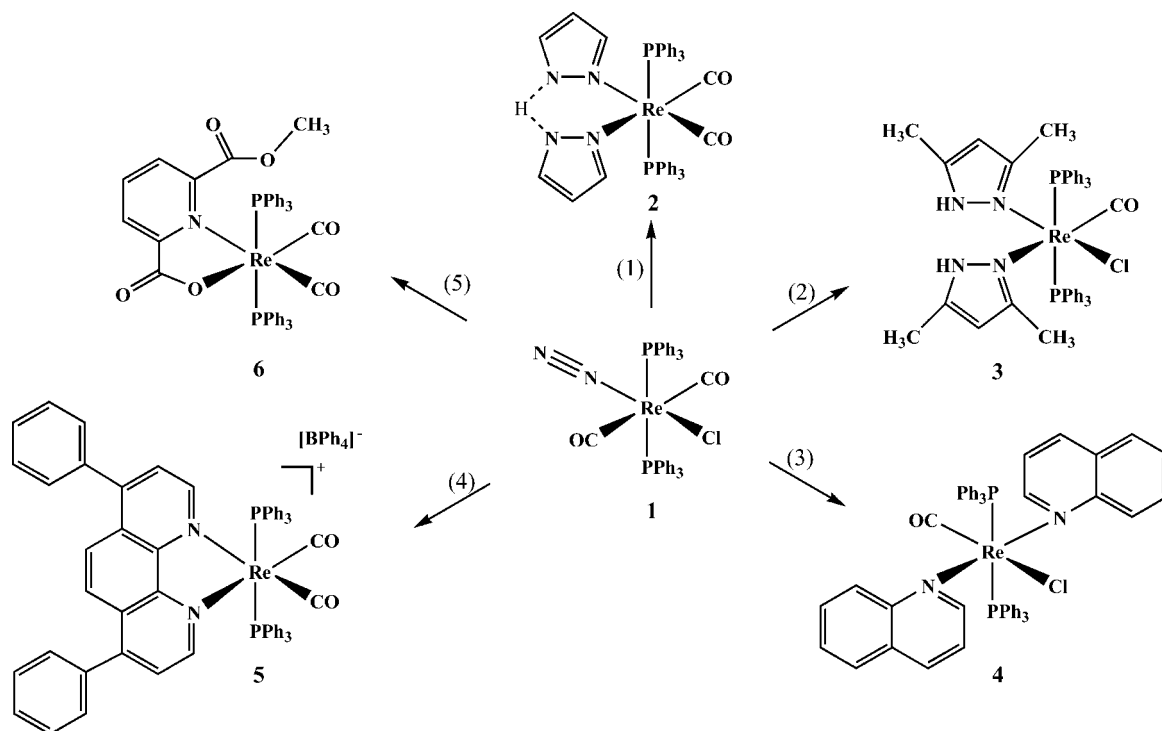
The reactions of the dinitrogen rhenium(I) complex $[\text{ReCl}(\text{N}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**1**) with the N-heterocycle ligands of Scheme 1 in refluxing methanol or a methanol/benzene mixture led to the displacement of the N_2/Cl^- ligands, or of the N_2 and one CO ligand in **1** (Scheme 2), thus allowing the formation of the new mono- and dicarbonyl rhenium(I) complexes $[\text{ReCl}(\text{L})_2(\text{CO})(\text{PPh}_3)_2]$ { $\text{L} = 3,5\text{-Me}_2\text{-Hpz}$ (**3**), quin (**4**)} and $[\text{Re}(\text{L})_n(\text{CO})_2(\text{PPh}_3)_2][\text{BPh}_4]_m$ { $\text{L} = \text{pz}/\text{Hpz}$, $n = 2$, $m = 0$ (**2**); $\text{L} = 4,7\text{-Ph}_2\text{-phen}$, $n = 1$, $m = 1$ (**5**); $\text{L} = 2\text{-Me-dipic}$ (2-methoxycarbonyl-6-pyridinecarboxylate), $n = 1$, $m = 0$ (**6**)}, which were isolated as air-stable crystalline solids in 78–44% yields. Hence, the reaction of **1** with pyrazole (Hpz, Scheme 2, reaction 1) gave the pale-yellow dicarbonyl complex $[\text{Re}(\text{pz})(\text{Hpz})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) with one pyrazolate (pz^-) ligand and one pyrazole (Hpz) ligand, formed upon N_2 and HCl elimination, while the use of 3,5-dimethylpyrazole (3,5-Me₂-Hpz, reaction 2) led to the displacement of N_2 and one CO ligand, yielding the yellow monocarbonyl dipyrazole compound $[\text{ReCl}(3,5\text{-Me}_2\text{-Hpz})_2(\text{CO})(\text{PPh}_3)_2]$ (**3**). The related deep-purple monocarbonyl complex $[\text{ReCl}(\text{quin})_2(\text{CO})(\text{PPh}_3)_2]$ (**4**) was obtained by treatment of the starting material **1** with an excess of quinoline (quin, Scheme 2, reaction 3). The reactions of 4,7-diphenyl-1,10-phenanthroline (4,7-Ph₂-phen) and dipicolinic (2,6-pyridinedicarboxylic) acid (H₂dipic) with **1** (reactions 4, 5) led to the deep-red ionic Re compound $[\text{Re}(4,7\text{-Ph}_2\text{-phen})(\text{CO})_2(\text{PPh}_3)_2][\text{BPh}_4]$ (**5**) (upon addition of $\text{Na}[\text{BPh}_4]$) and the orange neutral complex $[\text{Re}(2\text{-Me-dipic})(\text{CO})_2(\text{PPh}_3)_2]$ (**6**), respectively. The complexes **2–6** were characterized by IR spectroscopy, FAB-MS, ^1H -, $^{31}\text{P}\{^1\text{H}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, cyclic voltammetry, elemental analyses and single-crystal X-ray diffraction (for **2**, **5** and **6**) structural analyses.

Complex **2** bears both one Hpz ligand and its anionic conjugate base (pz^-). However, the ^1H - and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show their magnetic equivalence as accounting for a single set of resonances attributable to proton or carbon atoms of both ligands. In the ^1H NMR spectrum of **2**, the broad 1 H intensity NH signal at $\delta = 11.26$ ppm is assigned to $\text{N-H}\cdots\text{N}$, although the upfield shift relative to uncoordinated pyrazole [$\delta(\text{NH}) = 13.60$ ppm, CCl_4 (0.5 M)]^[12] cannot be directly related to the effects of the hydrogen bond and/or of a dynamic proton exchange since in other cases^[10a] they led to lowfield shifts. The solid-state IR spectrum of **2** exhibits an intense $\nu(\text{NH})$ band with a maximum at 3317 cm^{-1} , whose broad character is indicative of hydrogen bonding.

In contrast, both 3,5-Me₂-Hpz ligands are neutral in complex **3**. Its ^1H NMR spectrum shows a 2 H intensity NH signal at $\delta = 11.06$ ppm, which is also shifted upfield relative to free 3,5-dimethylpyrazole [$\delta(\text{NH}) = 12.29$ ppm, CDCl_3 (1.0 M)]^[12] while the IR spectrum of this compound exhibits a $\nu(\text{NH})$ band at 3222 cm^{-1} .

In complex **6** the dipicolinate ligand (2-Me-dipic) is bidentate, exhibiting N,O-coordination and one free arm whose esterification to give a methyl acetate moiety occurred during the synthesis in methanol solution, conceivably being promoted by the Re^{I} centre since the methyl ester was not detected in a blank experiment upon refluxing dipicolinic acid in methanol for several hours in the absence of a metal complex. The same type of esterification was previously observed^[6c] by us in the course of the synthesis of Re^{V} complexes such as $[\text{ReOCl}_2(2\text{-Me-dipic})(\text{PPh}_3)]$ and $[\text{ReOCl}\{(\text{OCH}_2\text{CH}_2)\text{N}(\text{CH}_2\text{COO})(\text{CH}_2\text{COOCH}_3)\}(\text{PPh}_3)]$ derived from dipicolinic and *N*-(2-hydroxyethyl)iminodiacetic acids, respectively. The presence of the methyl ester group in **6** is corroborated by the detection of the corresponding CH_3 resonances in the ^1H - ($\delta = 4.19$ ppm) and $^{13}\text{C}\{^1\text{H}\}$ ($\delta = 53.91$ ppm) NMR spectra. Moreover, the IR spectrum of **6** shows strong bands at 1740 and 1435 cm^{-1} associated with ν_{as} and ν_{s} vibrations, respectively, of the COOMe fragment.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the dicarbonyl complexes exhibit two CO signals, lying in the δ range of ca. 203–189 ppm for complexes **2** and **6**, whereas in **5** they are significantly shifted upfield to $\delta = 166.74$ and 166.04 ppm. In the monocarbonyl complex **3** the corresponding CO resonance is observed at $\delta = 197.80$ ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of all complexes **2–6** indicate the stereochemically favoured *trans* phosphane coordination in view of the single resonance detected in the δ range of ca. 32–20 ppm (relative to external H_3PO_4), which is shifted downfield from that ($\delta = -5.47$ ppm) of free triphenylphosphane. These signals and all other NMR resonances of complexes **2–6** are unexcep-



Scheme 2. (1): + Hpz – N₂ – HCl; (2): + 3,5-Me₂-Hpz – N₂ – CO; (3): + quin – N₂ – CO; (4): + 4,7-Ph₂-phen + Na[BPh₄] – N₂ – NaCl; (5): + H₂dipic – N₂ – HCl.

tional and comparable to those found in related rhenium complexes.^[6,10a,10e–g,13]

The IR spectra of the dicarbonyl complexes **2**, **5** and **6** exhibit two strong $\nu(\text{CO})$ bands in the 1929–1924 and 1853–1841 cm^{−1} ranges, similar to those of the starting material **1** (1921 and 1844 cm^{−1}) and other dicarbonyl Re^I complexes containing the *cis*-{Re(CO)₂} moiety, for example, [Re(L)(CO)₂(PPh₃)₂] {L = MeCOO or EtCOO;^[14a] OC(NH₂)S, OC(NHPh)S or OC(NHC₆H₄Me-4)S;^[14b] and [Re(L)(CO)₂(bipy)] {bipy = 2,2'-bipyridine, L = diethyl-2-(*N*-*p*-tolylimino)-3-(hydroxymethylene)butane-1,2-dicarboxylate}.^[14c] An additional $\nu(\text{CO})$ band is detected at 2032 cm^{−1} in the spectrum of **2**, as observed with other rhenium carbonyl complexes comprising pyrazole moieties.^[14d] Two strong $\nu(\text{CO})$ bands at 1922 and 1839 cm^{−1} are also shown by **3**, whereas in complex **4** the $\nu(\text{CO})$ band is detected at 1778 cm^{−1}, being considerably shifted to a lower-energy region more typical for a bridging carbonyl group.^[14e] Nevertheless, we believe that compound **4** is mononuclear and bears a terminal carbonyl ligand *trans* to the ligated Cl[−], as formulated in Scheme 2. This is in agreement with (i) an X-ray single-crystal diffraction analysis of **4** which indicates its basic and mononuclear structure, with the *trans*-CO/Cl arrangement, although with a too-high error to be reported, as well as with (ii) a FAB-MS(+) analysis which clearly detects the molecular ion [ReCl(quin)₂(CO)(PPh₃)₂]⁺ as the heaviest observed fragment (see later). A low IR $\nu(\text{CO})$ value (ca. 1800 cm^{−1})^[4e] was also found for the Re^I monocarbonyl complex *trans*-[ReCl(CO)(dppe)₂] with the strong electron-donor chloro ligand which

promotes the electron release from d_π orbitals of the metal to the π*(CO) orbitals, as it also conceivably occurs in complex **4**. This is also assisted by the limited π-electron acceptance of the two quinoline ligands in comparison with the CO and N₂ ligands in compound **1**. The IR spectra of complexes **3–6** also show a set of bands due to the ν_{as} and ν_{s} vibrations of CH groups in the typical 3060–3050 and 3000–2925 cm^{−1} ranges, respectively. The characteristic $\nu(\text{PPh})$ bands due to the PPh₃ ligands are observed at 747–743 and 697–695 cm^{−1}.

The positive FAB-MS spectra of compounds **3–6** exhibit the molecular ions [M]⁺ with the expected isotopic patterns at *m/z* values of 966, 1032, 1099 and 947, respectively, while the protonated molecular ion [M + H]⁺ is detected at *m/z* = 903 in the spectrum of **2**. Fragmentation pathways involve the stepwise loss of CO, Cl and PPh₃ ligands as well as of N-, N,N- or N,O-moieties. A comparative analysis of peak intensities concerned with typical fragmentations suggests that in complexes **3–6** the elimination of one PPh₃ ligand is a favourable process, in agreement with the detection of very intense signals assigned to the [M – PPh₃] (in **3**, **4**), [M – PPh₃ – 2CO] (in **5**) and [M – PPh₃ – CO] (in **6**) fragments. In contrast, the release of one or two pyrazole ligands is more favourable in **2** since a set of intense peaks attributed to the [M – pz], [M – pz – CO], [M – pz – Hpz] and [M – pz – Hpz – CO] fragments is observed. The presence of the [BPh₄][−] counterion in **5** is clearly confirmed by the negative FAB-MS spectrum (the intense signal of the [M][−] molecular ion at *m/z* = 319 with the expected isotopic pattern) and by the IR spectrum. Also, elemental analyses

of all compounds are consistent with the proposed formulations (Scheme 2) which are further confirmed by single-crystal X-ray diffraction studies (for **2**, **5** and **6**).

X-ray Crystal Structures

The molecular structures of complexes **2**, **5** and **6** are shown in Figures 1, 2 and 3, respectively, and selected bond lengths and angles are given in Table 1. All compounds crystallize in the monoclinic crystal system (space group $P2_1/n$) and exhibit a distorted octahedral coordination environment about rhenium filled by the N-, N,N- or N,O-ligand(s), two triphenylphosphane groups and two carbonyl groups.

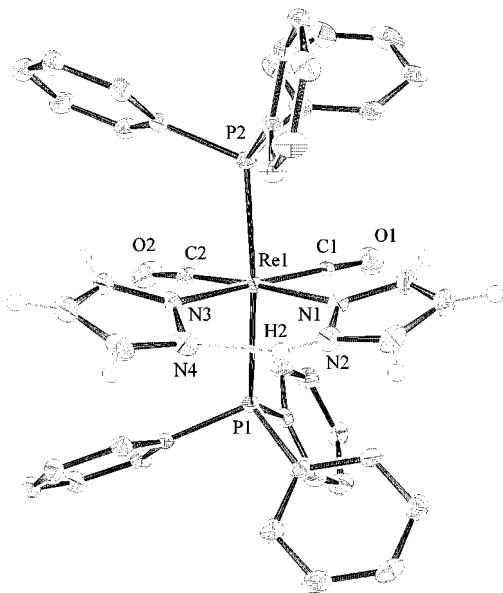


Figure 1. An ORTEP representation of **2** with ellipsoids shown at the 50% probability level. Phenyl hydrogen atoms are omitted for clarity.

The molecular structure of **2** (Figure 1) shows the pz^- and Hpz ligands *trans* to the carbonyl groups. The Re1-C1 and Re1-C2 bond lengths of 1.920(4) and 1.893(4) Å, respectively, are common for rhenium carbonyl complexes,^[10a,10d–g,15] while the carbonyl C1-O1 and C2-O2 distances of 1.141(5) and 1.162(5) Å, respectively, are comparable to the $\text{C}\equiv\text{O}$ bond of ca. 1.128 Å^[16] in molecular carbon monoxide. The binding of the Hpz/pz^- ligands to rhenium is characterized by a slight difference between the Re1-N1 [2.219(3) Å] and Re1-N3 [2.176(3) Å] bond lengths which agree with those reported for other rhenium carbonyl complexes comprising pyrazole or hydrotris(pyrazolyl)-borate $[\text{HB}(\text{pz})_3]^-$ derivatives, for example, $[\text{Re}(\text{pz})(\text{Hpz})_2(\text{CO})_3]$,^[10a] $[\text{Re}\{\text{HB}(\text{pz})_3\}(\text{CO})_2\text{L}]$ ($\text{L} = \text{THF}$ or PPh_3)^[15b] and $[\{\text{Re}(\text{B}(\text{Hpz})_3)(\text{CO})_2\}_2(\text{N}_2)]$.^[17] Although only one NH proton is crystallographically localized at one of the pyrazole moieties of **2**, its assignment to the N2 atom is rather formal and in reality it may be split between N2 and N4 . This agrees with the observation of a rather short $\text{N2}\cdots$

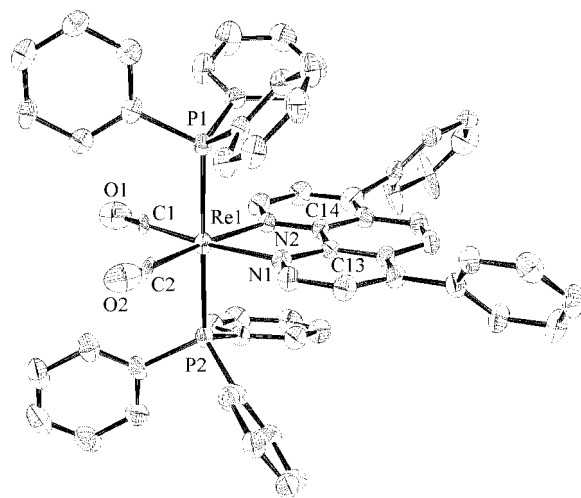


Figure 2. An ORTEP representation of the cationic part of **5** with ellipsoids shown at the 50% probability level. All hydrogen atoms and the solvent molecule are omitted for clarity.

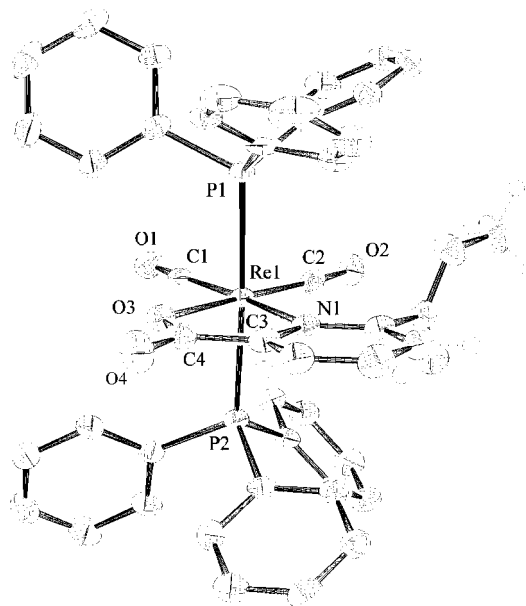


Figure 3. An ORTEP representation of **6** with ellipsoids shown at the 50% probability level. Phenyl hydrogen atoms and the solvent molecule are omitted for clarity.

$\text{H2}\cdots\text{N4}$ intramolecular hydrogen bond with $\text{N2}\cdots\text{N4}$ distance of 2.627(5) Å [N2-H2 0.94(4) Å and $\text{H2}\cdots\text{N4}$ 1.74(5) Å; $\text{N2-H2}\cdots\text{N4}$ 156(4)°], which connects two pyrazole groups forming the $\text{Re1-N1-N2}\cdots\text{N4-N3}$ ring with the N1-Re1-N3 angle of 89.22(12)°. Related features of the NH protons assignment and splitting, and the hydrogen-bonding interactions within the Hpz and pz^- fragments were observed in some Re, Ru, Co, Pd, Pt and Zn complexes.^[10a] The triphenylphosphane groups are bound almost linearly, and the Re-P distances range from 2.4251(10) to 2.4453(10) Å being comparable to those of compounds **5** and **6** and in accordance with those reported for other carbonyl rhenium complexes with *trans* PPh_3 ligands.^[14a,18]

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2**, **5** and **6**.

	2	5 ·0.5CH ₂ Cl ₂	6 ·EtOH
Re1–C1	1.920(4)	2.004(6)	1.918(6)
Re1–C2	1.893(4)	2.042(7)	1.887(7)
Re1–N1	2.219(3)	2.162(4)	2.216(4)
Re1–N2	–	2.147(4)	–
Re1–N3	2.176(3)	–	–
Re1–O3	–	–	2.176(4)
Re1–P1	2.4251(10)	2.4434(12)	2.4273(13)
Re1–P2	2.4453(10)	2.4439(13)	2.4246(13)
C1–O1	1.141(5)	0.977(6)	1.126(6)
C2–O2	1.162(5)	0.860(6)	1.167(7)
C1–Re1–C2	93.81(16)	95.5(2)	85.0(2)
C1–Re1–N1	85.54(13)	168.77(17)	172.8(2)
C1–Re1–N2	–	93.05(17)	–
C2–Re1–N1	176.20(14)	95.7(2)	102.1(2)
C2–Re1–N2	–	171.45(19)	–
C2–Re1–O3	–	–	176.63(18)
N1–Re1–N2	–	75.73(14)	–
N1–Re1–N3	89.22(12)	–	–
N1–Re1–O3	–	–	74.51(16)
C1–Re1–P1	90.65(11)	89.78(14)	89.19(14)
C2–Re1–P1	84.02(12)	90.66(17)	90.87(16)
C1–Re1–P2	91.66(11)	88.90(14)	89.18(14)
C2–Re1–P2	91.69(12)	91.74(17)	91.35(16)
N1–Re1–P1	92.24(9)	89.94(10)	90.37(11)
N1–Re1–P2	92.07(9)	90.90(10)	90.95(11)
P1–Re1–P2	175.26(3)	177.36(4)	177.13(5)
Re1–C1–O1	176.6(3)	179.2(6)	176.9(5)
Re1–C2–O2	175.8(4)	178.2(8)	176.1(5)

The major deviation from the octahedral geometry in **2** concerns the C2–Re1–P1 angle of 84.02(12)°; the other bond angles are relatively close to the idealized 90° and 180°.

Compound **5** is the first structurally characterized example with the 4,7-diphenyl-1,10-phenanthroline ligand within the large family of phenanthroline Re complexes. Its molecular structure comprises the [Re(4,7-Ph₂-phen)(CO)₂-(PPh₃)₂]⁺ cation and the [BPh₄][−] anion, with the separation between rhenium and boron centres being ca. 8.91 Å. The cationic part also contains two phosphane ligands in *trans* position, whereas the equatorial sites are occupied by the bidentate phenanthroline ligand and the two carbonyl groups (Figure 2). The octahedral environment around rhenium is more distorted than that of complex **2**, exhibiting a major deviation from an idealized geometry with a minimal N1–Re1–N2 angle of 75.73(14)°. The Re1–C1 and Re1–C2 bonds of 2.004(6) and 2.042(7) Å, respectively, are lengthened by ca. 0.10–0.15 Å relative to the corresponding distances in **2** and other complexes with a phenanthroline moiety.^[10d–g,15a] Such an elongation of the Re–C distances is concomitant with the shortening of the C1–O1 and C2–O2 bonds to 0.977(6) and 0.860(6) Å, respectively; the latter distance is unusually short and this is not reflected in ν(CO) which is comparable to the other complexes. The phenanthroline molecule is bound to the metal forming a N1–C13–C14–N2–Re1 chelate ring, and the Re1–N1 and Re1–N2 bonds of 2.162(4) and 2.147(4) Å, respectively, lie in the range of ca. 2.14–2.22 Å reported for other phenanthroline Re complexes.^[10d–g,15a]

The structure of **6** (Figure 3), with a chelating methyl-dipicolinate ligand, is similar to that of **2** comprising the pyrazolate/pyrazole ligands in the equatorial sites. In the monoesterified dipicolinate ligand, the nitrogen N1 is *trans* to the C1–O1 carbonyl group and the carboxylate oxygen O3 is *trans* to the C2–O2 ligand, forming a Re1–N1–C3–C4–O3 chelate ring with a N1–Re1–O3 bite angle of 74.51(16)° which is the most deviated angle from the idealized 90° around the distorted octahedral geometry of the Re1 centre. The bond lengths within the dipicolinate moiety in **6** are analogous to those of [ReBr{C₅H₃N-(COOEt)(COOMe)}(CO)₃]^[10i] and [ReOCl₂(2-Me-dipic)]^[6c] although the latter contains a rather short Re–O_{dipic} bond [2.037(2) Å] relative to the corresponding Re1–O3 distance of 2.176(4) Å in **6**. The Re1–C1 [1.918(6) Å] and Re1–C2 [1.887(7) Å] bonds as well as the C1–O1 [1.126(6) Å] and C2–O2 [1.167(7) Å] distances in **6** are standard and very close to those of **2** (Table 1) and other carbonyl rhenium complexes.^[10a,10d–g,15] In the structure of **6**·EtOH, O–H···O hydrogen-bonding interactions are observed between the dipicolinate oxygen O4 and the hydroxy group of the ethanol crystallization molecule [O99···O4 2.671(8) Å], as well as between two ethanol molecules from adjacent units [O99···O99 2.869(2) Å].

Electrochemical Studies

Complexes **2**, **3**, **5** and **6** exhibit, by cyclic voltammetry at a Pt electrode in 0.2 M [nBu₄N][BF₄]/CH₂Cl₂ solution, a first single-electron reversible (or quasireversible) (for **2** and **5**) or irreversible (for **3** and **6**) oxidation at ¹E_{1/2}^{ox} = 0.67 (**2**) and 1.22 (**5**) V or ¹E_p^{ox} = 0.75 (**3**) and 0.87 (**6**) V vs. SCE (Table 2, Figure 4 for **5**), assigned to the Re^I → Re^{II} oxidation, followed by a second reversible (for **2** and **3**) or irreversible (for **6**) oxidation at close potentials (1.00 to 1.15 V vs. SCE), most likely caused by the Re^{II} → Re^{III} oxidation. A third irreversible oxidation wave is also observed for compounds **2**, **3** and **6** at a higher potential (ca. 1.34–1.43 V vs. SCE). Complex **4** could not be studied by cyclic voltammetry because of its instability in the solvent/electrolyte medium.

For the quasireversible waves, increasing the scan rate from 0.2 to 0.5 or 1.0 V s^{−1} usually led to an enhancement of the degree of reversibility. The oxidation potentials of the neutral complexes **2**, **3** and **6** are lower than the corresponding potentials for the starting compound **1** (¹E_{1/2}^{ox} = 0.94, ¹E_p^{ox} = 1.79 V vs. SCE, measured^[6a] under identical experimental conditions). This confirms the stronger electron-donor character of the N- and N,O-ligands in **2**, **3** and **6** relative to ligated Cl[−] + N₂ or N₂ + CO in **1**, in agreement with the π-electron-acceptor character of N₂ and CO. The highest oxidation potential is observed for [Re(4,7-Ph₂-phen)(CO)₂(PPh₃)₂]⁺ in **5** (¹E_{1/2}^{ox} = 1.22 V vs. SCE) on account of its positive charge.

In addition, compounds **5** and **6** show (Table 2, Figure 4 for **5**) one reversible reduction wave at an unusually high potential (¹E_{1/2}^{red} = −0.01 and −0.18 V vs. SCE, respec-

Table 2. Cyclic voltammetric data for the Re^I complexes.^[a]

	^I <i>E</i> _{1/2} ^{ox} (^I <i>E</i> _p ^{ox})	^{II} <i>E</i> _{1/2} ^{ox} (^{II} <i>E</i> _p ^{ox})	(^{III} <i>E</i> _p ^{ox})	^I <i>E</i> _{1/2} ^{red}	^{II} <i>E</i> _{1/2} ^{red}
1 ^[b]	0.94	(1.79)	—	—	—
2 ^[c]	0.67	1.00	(1.41)	—	—
3 ^[d]	(0.75) ^[c]	1.00	(1.34)	—	—
5 ^[f]	1.22	—	—	−0.01	−1.21
6	(0.87)	(1.15) ^[e]	(1.43)	−0.18	−0.57

[a] Values given in V ± 0.02 vs. SCE (CH₂Cl₂/[nBu₄N][BF₄], *v* = 0.2 V s^{−1}, for further details see Exp. Sect.); *E*_{1/2} corresponds to half-wave potential of reversible or quasireversible wave; peak potentials (*E*_p) for irreversible waves are given in brackets. [b] Included for comparison with ref.^[6a] [c] Two new reduction waves at *E*_p^{red} = −0.30 V and *E*_{1/2}^{red} = −0.79 V (not observed in initial oxidation and reduction scans) appeared over time, conceivably caused by decomposition products. [d] Two new reduction waves at *E*_{1/2}^{red} = −0.21 V and *E*_{1/2}^{red} = −0.70 V (not observed in initial oxidation and reduction scans) appeared over time, conceivably caused by decomposition products. [e] This wave becomes quasireversible at higher scan rates (*v* = 0.5 or 1.0 V s^{−1}). [f] An additional wave was observed at *E*_p^{ox} = 0.97 V as a result of the oxidation of the counterion [BPh₄][−].

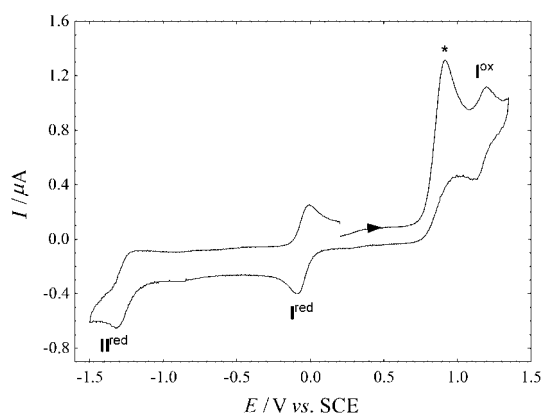


Figure 4. Cyclic voltammogram of [Re(4,7-Ph₂-phen)(CO)₂(PPh₃)₂][BPh₄] (**5**) (8.5 × 10^{−4} mol L^{−1}), in 0.2 M [nBu₄N][BF₄]/CH₂Cl₂, at a Pt working electrode and at a scan rate of 0.2 V s^{−1}; * wave due to the oxidation of the counterion [BPh₄][−].

tively), followed by a second quasireversible reduction wave at ^{II}*E*_{1/2}^{red} = −1.21 (**5**) and −0.57 (**6**) V vs. SCE. The evidence for considering the wave at *E*_{1/2} = −0.01 V vs. SCE in compound **5** as a reduction wave is apparent from its position in the *I* (current) scale in the cyclic voltammogram (Figure S1 in the Supporting Information). Further proof is provided by controlled potential electrolysis (CPE) at a potential slightly lower than that of *I*^{red} (i.e., at −0.30 V), which led to a colour change of solution (i.e., from deep brown to light green), while neither alteration in colour was detected nor charge was measured upon attempted CPE at a potential above that of the same wave.

According to literature data for other Re^I compounds with aromatic N-heterocycle ligands^[7b,19–22] (e.g., [{ReCl(CO)₃}(ddpq)]⁺ {ddpq = 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline}, [Re(bpa)(bqu)(CO)₃]⁺ {bpa = 1,2-bis(4-pyridyl)ethane, bqu = 2,2′-biquinoline}, [Re(bpy)(4,4′-bpy)(CO)₃]⁺ {bpy = 2,2′-bipyridine, 4,4′-bpy = 4,4′-bipyridine}, etc.),^[19,20] the waves (one or two) observed at less negative potentials (i.e., from −0.2 to −1.1 V vs. SCE)

are expected to correspond to N,N(N,O)-ligand-centred reductions, whereas the waves at more negative potentials can be assigned to the Re^I → Re⁰ reduction. Although our measured less-negative potentials are considerably higher than most of those in the literature, they are comparable to, for example, *E*_{1/2}^{red} = −0.24 V vs. SCE reported for a ligand-centred process in [{Re(CO)₃(CH₃CN)₂(ppz)]²⁺ (ppz = 4′,7′-phenanthroline-5′,6′:5,6-pyrazine).^[20] However, one should mention that the free 4,7-Ph₂-phen species does not show any waves in the window from −2.0 to +2.0 V vs. SCE.

The possible ligand-centred character of the *I*^{red} wave (Figure 4) is also supported by the UV/Vis spectrum of **5** recorded in CH₂Cl₂ solution, which reveals the presence of a rather broad and intense (*ε* ≈ 9200 L mol^{−1} cm^{−1}) band with a maximum at ca. 400 nm, most likely related to a metal-to-ligand charge-transfer (MLCT) process and in agreement with reported data for Re^I systems with polypyridyl ligands.^[7b,20–22] For example, MLCT bands with a rather close absorption maximum and intensity have been observed for [Re(bpy)(py)(CO)₂{P(OEt)₃}]⁺[PF₆][−] (bpy = 2,2′-bipyridine, py = pyridine) (*λ*_{max} = 397 nm), [Re(bpy)(CO)₂(PPh₃)₂]⁺[PF₆][−] (*λ*_{max} = 401 nm), [Re{(CF₃)₂-bpy}(CO)₂{P(OEt)₃}]⁺[PF₆][−] {(CF₃)₂-bpy = 4,4′-bis(trifluoromethyl)bipyridine} (*λ*_{max} = 404 nm) and [ReCl(bppz)(CO)₃]⁺ {bppz = 2,3-bis(2-pyridyl)pyrazine} (*λ*_{max} = 417 nm).

The measured first oxidation potential (upon conversion to the NHE scale) for the rhenium(I) complex [Re(4,7-Ph₂-phen)(CO)₂(PPh₃)₂]⁺ in **5** (^I*E*_{1/2}^{ox} = 1.22 V vs. SCE, i.e., 1.22 + 0.245^[11] = 1.47 V vs. NHE) was applied to calculate the electrochemical Lever *E*_L parameter^[11,23] for the 4,7-Ph₂-phen ligand according to the Lever's equation (1), valid for octahedral complexes, where Σ*E*_L is the sum of the *E*_L values for all the ligands, and *S*_M and *I*_M are standard parameters dependent on the metal redox couple, spin state and stereochemistry.^[11]

$$E = S_M(\Sigma E_L) + I_M, \text{ V vs. NHE} \quad (1)$$

Thus, applying the corresponding *S*_M = 0.76 and *I*_M = −0.95 V vs. NHE values for the Re^{II/I} couple^[11b] and the *E*_L values for the CO and PPh₃ ligands (*E*_L = 0.99 and 0.39 V vs. NHE, respectively),^[11a,23] we have estimated, for the first time, the value of the electrochemical Lever ligand parameter, *E*_L = 0.21 V vs. NHE, for each binding arm of the 4,7-Ph₂-phen ligand. This value is comparable to those previously established^[11a,23] for monodentate 1,10-phenanthroline (*E*_L = 0.26 V vs. NHE) and 4,7-dimethyl-1,10-phenanthroline (*E*_L = 0.23 V vs. NHE) ligands.

Conclusions

This study shows that the mixed dinitrogen-dicarbonyl complex [ReCl(N₂)(CO)₂(PPh₃)₂] (**1**) constitutes a convenient starting material for the synthesis of new low-oxidation-state Re complexes bearing N-, N,N- or N,O-ligands with unsaturated N-heterocycle groups coordinated to {Re(CO)} or {Re(CO)₂} centres. It is thus possible to open

a suitable entry to mono- and dicarbonyl Re complexes with such types of ligands, allowing the extension to the $\{\text{Re}(\text{CO})_n\}$ ($n = 1$ or 2) centres of the rich coordination chemistry that is being developed for complexes with the tricarbonyl $\{\text{Re}(\text{CO})_3\}$ site^[8] which has found applications in various fields such as nuclear medicine, pharmacology, photoluminescent materials, supramolecular chemistry and catalysis.^[7a,9]

It is also necessary to mention that the axial bisphosphane *trans*- $\{\text{Re}(\text{PPh}_3)_2\}^+$ core in complex **1** remains during the substitution reactions which involve only the equatorial $\text{N}_2/\text{CO}/\text{Cl}^-$ ligands. The observed behaviour can be accounted for by a combination of various factors, namely the usual lability of the dinitrogen ligand (a rather weak σ -electron donor),^[24] the labilization of the chloro ligand upon loss of N_2 (a π -electron acceptor that, when *trans* to Cl^- , enhances the electron release from the latter to the metal), the strong *trans* influence of the effective π -acceptor CO ligands in *trans* position (with their resulting mutual labilization), the protic-acid character of the new ligand precursor and the chelating effect of a possible bidentate new ligand.

Hence, on reactions of **1** with acidic N-heterocycle ligands (pyrazole or dipicolinic acid, reactions 1 and 5, respectively), N_2 and Cl^- are the replaced ligands (the substitution of the latter being assisted by protonation), whereas the reactions of **1** with nonacidic and nonchelating N-heterocycle ligands (3,5-dimethylpyrazole and quinoline, reactions 2 and 3, respectively) occur by displacement of N_2 and one CO ligand. Chelation of the new ligand(s) leads to CO *trans*-to-*cis* isomerization with the formation of *cis*-dicarbonyl products (reactions 1, 4 and 5) from the *trans*-dicarbonyl starting complex **1**. However, *cis*- to *trans*-Cl/CO isomerization can occur (reaction 3) with a nonchelating bulky ligand, resulting in a particularly favourable π -donor/ π -acceptor interaction between the former ligands (compound **4**).

The synthetic significance of those observations, namely in terms of selectivity, deserves further exploration, by taking advantage of the versatile structural/electronic features of the mixed N_2/CO complex **1** as demonstrated in this study.

Experimental Section

General Materials and Procedures

All synthetic work was performed under dinitrogen using standard Schlenk techniques. The solvents were dried and degassed by standard methods. Potassium perrhenate (Merck), triphenylphosphane (Aldrich), benzoylhydrazine (Aldrich), carbon monoxide (Air Products), pyrazole (Aldrich), 3,5-dimethylpyrazole (Aldrich), quinoline (Merck), 4,7-diphenyl-1,10-phenanthroline (Aldrich), sodium tetraphenylborate (Aldrich) and 2,6-pyridinedicarboxylic acid (Aldrich) were obtained from commercial sources and used as received. $[\text{ReCl}(\text{N}_2)(\text{CO})_2(\text{PPh}_3)_2]$ (**1**) was prepared by a published method.^[1g]

C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. The FAB mass

spectra were obtained with a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (*m*-NBA) matrices of the samples with 8 keV (ca. $1.18 \cdot 10^{15}$ J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded with a Jasco FT/IR-430 instrument in KBr pellets. ^1H -, $^{31}\text{P}\{^1\text{H}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured with a Varian UNITY 300 spectrometer at ambient temp. The ^{31}P chemical shifts are relative to external 85% H_3PO_4 aqueous solution. UV/Vis spectra were recorded with a Jasco model 7800 UV/Vis spectrophotometer.

The electrochemical experiments were carried out with an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry (CV) studies were undertaken in a two-compartment three-electrode cell, at platinum-wire working electrode ($d = 0.5\text{ mm}$) and counter electrodes, in 0.2 M $[\text{nBu}_4\text{N}][\text{BF}_4]/\text{CH}_2\text{Cl}_2$ solution. A Luggin capillary connected to a silver-wire pseudoreference electrode was used to control the working electrode potential. Controlled potential electrolysis (CPE) experiments were carried out in electrolyte solutions with the mentioned composition, in a two-compartment three-electrode cell with platinum-gauze working electrode and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudoreference electrode. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring that no significant potential drift occurred along the electrolyses. The oxidation potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the SCE by using the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ ($E_{1/2}^{\text{ox}} = 0.525\text{ V}$ vs. SCE) redox couple in 0.2 M $\text{CH}_2\text{Cl}_2/[\text{Bu}_4\text{N}][\text{BF}_4]$ solution.^[25] The obtained potentials vs. SCE can be converted into the NHE scale by addition of 0.245 V .^[11]

$[\text{Re}(\text{pz})(\text{Hpz})(\text{CO})_2(\text{PPh}_3)_2]$ (2**):** A mixture of **1** (50 mg, 0.060 mmol) and pyrazole (41 mg, 0.60 mmol) was refluxed in MeOH (20 mL) for 2 d to produce a brown suspension. It was filtered off, washed with MeOH ($3 \times 10\text{ mL}$), C_6H_6 ($3 \times 5\text{ mL}$) and Et_2O ($3 \times 10\text{ mL}$) and dried in vacuo to yield complex **2** as a pale-yellow microcrystalline solid. Yield: 78% (42 mg), based on **1**. Further purification of **2** can be achieved by recrystallization from a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_6/\text{EtOH}$ mixture. $\text{C}_{44}\text{H}_{36}\text{N}_4\text{O}_2\text{P}_2\text{Re}$ (901.9): calcd. C 58.59, H 4.13, N 6.21; found C 58.27, H 4.21, N 5.89. FAB-MS(+): $m/z = 903$ $[\text{M} + \text{H}]^+$, 835 $[\text{M} - \text{pz}]^+$, 807 $[\text{M} - \text{pz} - \text{CO}]^+$, 778 $[\text{M} - \text{Hpz} - 2\text{CO}]^+$, 767 $[\text{M} - \text{pz} - \text{Hpz}]^+$, 739 $[\text{M} - \text{pz} - \text{Hpz} - \text{CO}]^+$, 709 $[\text{Re}(\text{PPh}_3)_2 - 2\text{H}]^+$, 613 $[\text{M} - \text{PPh}_3 - \text{CO} + \text{H}]^+$, 449 $[\text{RePPh}_3]^+$. IR (KBr): $\tilde{\nu} = 3317$ (s br) $\nu(\text{NH})$, 3148 (w) $\nu_{\text{as}}(\text{CH})$ and 3055 (w) $\nu_{\text{s}}(\text{CH})$, 2032 (m), 1924 (s) and 1841 (s) $\nu(\text{CO})$, 743 (s) and 697 (s) $\nu(\text{PPh})\text{ cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 11.26$ (s br, 1 H, NH), 7.81 [m, 2 H, $\text{pzH}(3/5)$], 7.68–7.50 (m, 12 H, PPh_3), 7.45–7.30 (m, 18 H, PPh_3), 6.81 [d, $J = 2.0\text{ Hz}$, 2 H, $\text{pzH}(3/5)$], 5.88 [t, $J = 2.1\text{ Hz}$, 2 H, $\text{pzH}(4)$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 202.86$ and 202.04 (CO), 142.15 (pzC), 134.75–134.30 (m, PPh_3), 133.91 (pzC), 129.77 (d, $J_{\text{CP}} = 9.4\text{ Hz}$, PPh_3), 128.70–128.35 (m, PPh_3), 107.61 (pzC) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 20.75$ (s) ppm. X-ray-quality crystals of **2** were grown by slow evaporation at 5°C of a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_6/\text{EtOH}$ solution of **2**.

$[\text{ReCl}(3,5\text{-Me}_2\text{-Hpz})_2(\text{CO})(\text{PPh}_3)_2]$ (3**):** A mixture of **1** (50 mg, 0.060 mmol) and 3,5-dimethylpyrazole (58 mg, 0.60 mmol) was refluxed in MeOH (20 mL) for 2.5 d to produce a brown-yellow cloudy solution. The solid was filtered off, washed with MeOH ($3 \times 10\text{ mL}$) and Et_2O ($3 \times 10\text{ mL}$) and dried in vacuo to yield complex **3** as a yellow microcrystalline solid. Further purification of **3** can be achieved by recrystallization from a $\text{C}_6\text{H}_6/\text{EtOH}(\text{MeOH})$

solution. Yield: 67% (39 mg), based on **1**. $C_{47}H_{46}ClN_4OP_2Re$ (966.5): calcd. C 58.41, H 4.80, N 5.80; found C 58.08, H 4.56, N 5.50. FAB-MS(+): m/z = 966 $[M]^+$, 834 $[M - \{3,5-Me_2-Hpz\} - Cl - H]^+$, 802 $[M - 2\{3,5-Me_2-Hpz\} + CO]^+$, 774 $[M - 2\{3,5-Me_2-Hpz\}]^+$, 746 $[M - 2\{3,5-Me_2-Hpz\} - CO]^+$, 739 $[M - 2\{3,5-Me_2-Hpz\} - Cl]^+$, 704 $[M - PPh_3]^+$, 668 $[M - PPh_3 - Cl - H]^+$, 640 $[M - PPh_3 - Cl - CO - H]^+$, 608 $[M - PPh_3 - \{3,5-Me_2-Hpz\}]^+$, 580 $[M - PPh_3 - \{3,5-Me_2-Hpz\} - CO]^+$, 531 $[M - PPh_3 - \{3,5-Me_2-Hpz\} - Ph]^+$, 512 $[M - PPh_3 - 2\{3,5-Me_2-Hpz\}]^+$, 503 $[M - PPh_3 - \{3,5-Me_2-Hpz\} - CO - Ph]^+$, 484 $[M - PPh_3 - 2\{3,5-Me_2-Hpz\} - CO]^+$, 407 $[M - 2PPh_3 - Cl - 2H]^+$, 329 $[M - PPh_3 - 2\{3,5-Me_2-Hpz\} - CO - 2Ph - H]^+$. IR (KBr): $\tilde{\nu}$ = 3222 (s) $\nu(NH)$, 3059 (w) $\nu_{as}(CH)$, 3002 (w) and 2925 (w) $\nu_s(CH)$, 1922 (s) and 1839 (s) $\nu(CO)$, 1571 (m) $\nu(C=N)$, 746 (m) and 695 (s) $\nu(PPh)$ cm^{-1} . 1H NMR ($CDCl_3$): δ = 11.06 (s, 2 H, NH), 7.65–7.10 (m, 30 H, PPh_3), 5.34 (s, 2 H, pzH), 1.76–1.56 (m, 12 H, $pzCH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 197.80 (CO), 152.44 and 139.74 (pzC), 134.90–134.20 (m, PPh_3), 129.82 (s, PPh_3), 128.60–128.30 (m, PPh_3), 107.76 (pzC), 15.95 and 11.44 ($pzCH_3$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.04 (s) ppm.

[ReCl(quin)₂(CO)(PPh₃)₂] (4): Complex **1** (50 mg, 0.060 mmol) was refluxed in a quinoline (0.50 mL) and methanol (20 mL) mixture for 15 h to produce a deep-brown cloudy solution. The solid was filtered off, washed with MeOH (5 $\times$ 10 mL) and Et₂O (3 $\times$ 10 mL) and dried in vacuo to yield complex **4** as a deep-purple microcrystalline solid. Yield: 70% (43 mg), based on **1**. $C_{55}H_{44}ClN_2OP_2Re$ (1032.6): calcd. C 63.98, H 4.30, N 2.71; found C 63.66, H 4.63, N 2.72. FAB-MS(+): m/z = 1032 $[M]^+$, 770 $[M - PPh_3]^+$, 641 $[M - PPh_3 - quin]^+$, 613 $[M - PPh_3 - quin - CO]^+$, 484 $[M - PPh_3 - 2quin - CO]^+$. IR (KBr): $\tilde{\nu}$ = 3051 (m) $\nu_{as}(CH)$, 3000 (w) $\nu_s(CH)$, 1778 (s) $\nu(CO)$, 745 (s) and 695 (s) $\nu(PPh)$ cm^{-1} . 1H NMR ($CDCl_3$): δ = 7.71–7.40, 7.33–7.12 and 7.06–6.92 (m, 10 H + 18 H + 16 H, PPh_3 + $quinH$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 30.79 (s) ppm. No reliable $^{13}C\{^1H\}$ NMR spectrum could be accumulated because of the gradual decomposition of **4** in $CDCl_3$ or $[D_6]acetone$. Single crystals were grown by slow evaporation at 5 °C of a $CH_2Cl_2/Me_2CO(EtOH)$ solution of **4**. The proposed formulation of **4** with the *trans*-CO/Cl arrangement was also confirmed by a single-crystal X-ray diffraction analysis, but with a rather high error due to a heavy disorder.

[Re(4,7-Ph₂-phen)(CO)₂(PPh₃)₂][BPh₄] (5): A mixture of **1** (50 mg, 0.060 mmol) and 4,7-diphenyl-1,10-phenanthroline (60 mg, 0.18 mmol) was refluxed in a MeOH (10 mL) and C_6H_6 (20 mL) mixture overnight. The resulting deep-green clear solution was concentrated under reduced pressure to give a green oil which was dissolved in EtOH (15 mL) and treated with an ethanol solution (30 mL) of Na[BPh₄] (205 mg, 0.60 mmol). The obtained deep-green suspension was almost completely dissolved upon addition of acetone (30 mL). The resulting green clear solution was filtered and left to evaporate in air in a beaker at ambient temp. Deep-red crystals formed in a few days from that green solution. They were isolated by filtration, washed gently with Et₂O, collected and dried in vacuo to yield compound **5**. Yield: 64% (54 mg), based on **1**. $C_{86}H_{66}BN_2O_2P_2Re$ (1418.4): calcd. C 72.82, H 4.69, N 1.97; found C 72.47, H 4.86, N 2.25. FAB-MS(+): m/z = 1099 $[M]^+$, 1071 $[M - CO]^+$, 837 $[M - PPh_3]^+$, 808 $[M - PPh_3 - CO - H]^+$, 781 $[M - PPh_3 - 2CO]^+$, 767 $[M - \{4,7-Ph_2-phen\}]^+$, 739 $[M - \{4,7-Ph_2-phen\} - CO]^+$, 703 $[M - PPh_3 - 2CO - Ph - H]^+$, 625 $[M - PPh_3 - 2CO - 2Ph - 2H]^+$. FAB-MS(–): m/z = 319 $[BPh_4]^-$. IR (KBr): $\tilde{\nu}$ = 3054 (m br) $\nu_{as}(CH)$, 2999 (w) and 2983 (w) $\nu_s(CH)$, 1927 (s) and 1852 (s) $\nu(CO)$, 744 (s) and 697 (s) $\nu(PPh)$ cm^{-1} . 1H NMR ($CDCl_3$): δ = 7.90–6.40 (m, 66 H, PPh_3 + BPh_4 + $phenH$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 166.04 and 164.74 ($C=O$), 140.15 (m), 137.08,

133.24 (m), 130.97, 130.18 (d, J_{CP} = 6.0 Hz), 129.32 (m), 126.62 (m), 126.09 (m) and 122.17 (PPh_3 + BPh_4 + $phenC$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 22.51 (s) ppm. X-ray-quality crystals of **5**·0.5 CH_2Cl_2 were grown by slow evaporation of an EtOH/ Me_2CO/CH_2Cl_2 solution of **5**.

[Re(2-Me-dipic)(CO)₂(PPh₃)₂] (6): To a solution of **1** (50 mg, 0.060 mmol) in MeOH (20 mL) and C_6H_6 (10 mL) was added an excess of 2,6-pyridinedicarboxylic acid (108 mg, 0.60 mmol), and the reaction mixture was refluxed for 1 d. The resulting deep-orange clear solution was concentrated under reduced pressure to give an orange oil which was treated with MeOH (15 mL). The solid that separated out from the resulting solution was filtered off and discarded. The filtrate was evaporated under reduced pressure giving an orange oily solid to which Et₂O (30 mL) was added to form an orange precipitate. It was filtered off, washed with Et₂O (3 $\times$ 10 mL) and dissolved on a filter in Me_2CO (5 mL) to form a deep-orange solution which was taken to dryness under reduced pressure yielding an orange oil. Further addition of Et₂O (30 mL) led to the formation of a solid which was filtered off, washed with Et₂O (3 $\times$ 10 mL) and dried in vacuo to give complex **6** as an orange microcrystalline material. Yield: 44% (25 mg), based on **1**. $C_{46}H_{36}NO_6P_2Re$ (946.9): calcd. C 58.35, H 3.83, N 1.48; found C 58.03, H 3.49, N 1.84. FAB-MS(+): m/z = 947 $[M]^+$, 919 $[M - CO]^+$, 767 $[M - \{2-Me-dipic\}]^+$, 739 $[M - \{2-Me-dipic\} - CO]^+$, 657 $[M - PPh_3 - CO]^+$, 642 $[M - PPh_3 - CO - Me]^+$, 629 $[M - PPh_3 - 2CO]^+$, 614 $[M - PPh_3 - 2CO - Me]^+$, 505 $[M - PPh_3 - \{2-Me-dipic\}]^+$, 447 $[RePPh_3 - 2H]^+$. IR (KBr): $\tilde{\nu}$ = 3058 (m) $\nu_{as}(CH)$, 2954 (w) $\nu_s(CH)$, 1929 (s) and 1853 (s) $\nu(CO)$, 1740 (s) $\nu_{as}(COOMe)$, 1692 (s) $\nu_{as}(COO)$, 1482 (m) $\nu_s(COO)$, 1435 (s) $\nu_s(COOMe)$, 747 (s) and 696 (s) $\nu(PPh)$ cm^{-1} . 1H NMR ($CDCl_3$): δ = 8.59 (t, J = 7.9 Hz, 1 H, pyH), 8.49 (t, J = 7.8 Hz, 1 H, pyH), 8.30 (m, 1 H, pyH), 7.91–7.32 (m, 30 H, PPh_3), 4.19 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 208.54 and 189.24 (CO), 166.31 (COO), 153.53 (COOMe), 140.27, 139.08, 132.37, 131.62 and 127.65 (pyC), 134.83 (d, J_{CP} = 9.3 Hz), 134.42–134.26 (m), 130.25 and 129.63–128.30 (m, PPh_3), 53.91 (CH_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 31.96 (s) ppm. X-ray-quality crystals of **6**·EtOH were grown by slow evaporation at 5 °C of an EtOH/ Me_2CO or EtOH/ C_6H_6 solution of **6**.

X-ray Crystal Structure Determinations: The X-ray diffraction data of **2**, **5** and **6** were collected with a Nonius Kappa CCD diffractometer using Mo- K_α radiation. The Denzo-Scalepack^[26] program package was used for cell refinements and data reductions. All structures were solved by direct methods using the SHELXS-97,^[27] SIR97^[28] or SIR2002^[29] programs with the WinGX^[30] graphical user interface. An empirical absorption correction was applied to all data (T_{max}/T_{min} : 0.6242/0.5545, 0.8965/0.5149, 0.5172/0.7256 for **2**, **5** and **6**, respectively) using SORTAV^[31] or XPREP in SHELXTL v.6.14–1^[32] program. Structural refinements were carried out with SHELXL-97.^[33] In **2** the NH hydrogen atom was located from the difference Fourier map and refined isotropically. In **5** one of the phenyl groups in 4,7- Ph_2 -phen is disordered over two sites with occupancies 0.72 and 0.28. In these groups the aromatic rings were refined with fixed C–C distances of 1.39 Å. Moreover, the disordered CH_2Cl_2 solvent molecule was modelled by placing the two chlorines over three sites with equal occupancies. The solvent was partially lost from the structure, and all in all only half a molecule of CH_2Cl_2 was introduced into the structure. Because of the disorder, CH_2Cl_2 was refined only isotropically and the hydrogen atoms were omitted. In **6** the carbon atoms of the EtOH molecule are disordered over two sites with occupancies 0.55 and 0.45. The OH hydrogen atom of EtOH was located from the difference Fourier map but not refined (U_{iso} = 0.12). Other hydro-

Table 3. Crystal data and structure refinement details for complexes **2**, **5** and **6**.

	2	5 ·0.5CH ₂ Cl ₂	6 ·EtOH
Empirical formula	C ₄₄ H ₃₇ N ₄ O ₂ P ₂ Re	C _{86.5} H ₆₇ BClN ₂ O ₂ P ₂ Re	C ₄₈ H ₄₂ NO ₇ P ₂ Re
Formula weight	901.92	1460.82	992.97
Temperature [K]	120(2)	120(2)	120(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	11.5079(2)	14.7466(3)	10.0823(2)
<i>b</i> [Å]	16.6886(3)	14.7938(2)	11.9229(2)
<i>c</i> [Å]	19.7901(3)	32.5113(6)	35.7524(7)
α [°]	90	90	90
β [°]	99.4790(10)	97.335(8)	91.1040(10)
γ [°]	90	90	90
<i>V</i> [Å ³]	3748.81(11)	7034.6(2)	4297.01(14)
<i>Z</i>	4	4	4
$\rho_{\text{calcd.}}$ [Mg m ⁻³]	1.598	1.379	1.535
$\mu(\text{Mo-}K_{\alpha})$ [mm ⁻¹]	3.371	1.862	2.955
Number of collected reflections	40567	72404	24191
Number of unique reflections	8585	12266	7372
<i>R</i> _{int}	0.0584	0.0836	0.0586
Final <i>R</i> ₁ , [^a] <i>wR</i> ₂ [^b] (<i>I</i> ≥ 2σ)	0.0289, 0.0617	0.0430, 0.0926	0.0368, 0.0868
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0490, 0.0864	0.0696, 0.1034	0.0525, 0.0947
GOF on <i>F</i> ²	1.127	1.048	1.063
Largest diff. peak and hole [e Å ⁻³]	0.844, -2.736	1.467, -0.965	1.560, -1.088

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

gen atoms were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 3.

CCDC-623918 to -623920 (for **2**, **5**·0.5CH₂Cl₂ and **6**·EtOH, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Supplementary figure (Figure S1) showing the cyclic voltammogram of **5** initiated by the anodic and cathodic sweep.

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