Synthesis of Rhenium Carbonyl Complexes Bearing Substituted Pyrrolyl Ligands

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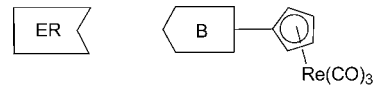
Summary: The formation of rhenium carbonyl complexes incorporating substituted pyrrolyl ligands was studied: the η^5 coordination mode of the pyrrolyl motif was not favored, while several bidentate monosubstituted pyrrolyl rhenium complexes were synthesized. It was shown that these species easily lose one carbonyl in refluxing THF or in the presence of triphenylphosphine.

Our interest in bioorganometallic chemistry,[1] and in particular in the design of new potential radiopharmaceuticals incorporating rhenium,[2] led us and others to the synthesis of complexes based on the association of a robust, low-valent, and relatively unhindered cyclopentadienyltricarbonylrhenium unit with biomolecules (Scheme 1) known for their capability for binding to estrogen receptors (ERα and ERβ).[3]

In order to find new species of biological interest, and to explore new synthetic routes in the field of organometallic chemistry, we envisaged a modification of the nature of the cyclopentadienyl link between the biomolecule and the metal. For that purpose, the corresponding isoelectronic pyrrolyl group has emerged as a good candidate, principally due to the large occurrence of the pyrrole motif in natural products[4] but also because of the interest in its use in the field of organometallic chemistry.[5] The use of this ligand for the synthesis of organometallic species of rhenium has not been widely studied (Scheme 2). Gladysz et al. reported[6] the first η^1-pyrrolyl-*C* complex **1**, prepared from the corresponding η^1-pyrrolyl-*N* species. A few other examples, such as compounds **2** and **3**, were respectively described by the groups of Bergman[7] and Harman.[8] The η^5 coordination mode between the pyrrolyl ring and the rhenium atom has been rarely encountered in the literature. Felkin and Zakrzewski[9] were pioneers in this field with the synthesis of **4**, while compound **5**, reported by Ziegler et al.,[10] is the only example of a rhenium complex incorporating both carbonyl ligands and an η^5-pyrrolyl ring.

The presence of voluminous ligands such as phosphines, tetramethylpyrrolyl, and tris(pyrazolyl)borate (Tp) in these examples is a handicap for the design of species as potential

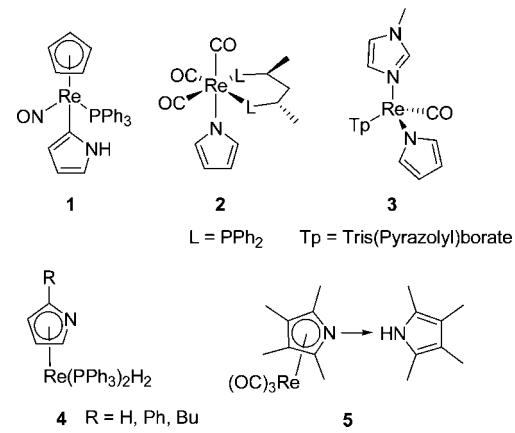
Scheme 1. Design of Potential Radiopharmaceuticals Incorporating the Cyclopentadienyltricarbonylrhenium Group



ER = Estrogen Receptors

B = Biomolecule (steroid, drug, antibodies...)

Scheme 2. Examples of Organometallic Complexes of Rhenium Bearing Pyrrolyl or Substituted Pyrrolyl Ligands



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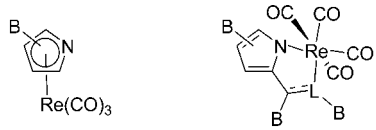
Scheme 3. Design of Potential Radiopharmaceuticals Incorporating a Substituted Pyrrolyl Tricarbonylrhenium or Tetracarbonylrhenium Group

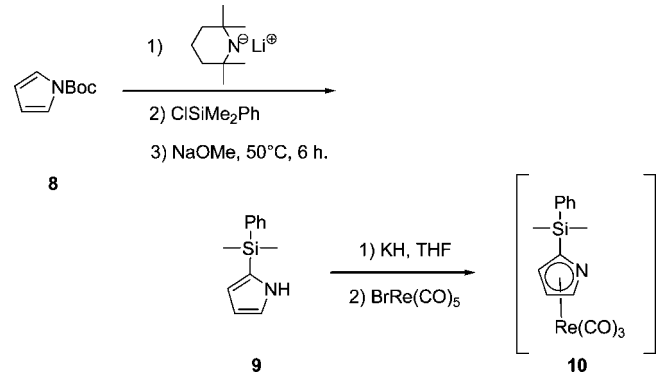


radiopharmaceuticals when one has to consider the necessity of strong binding to the receptor studied. The less hindered carbonyl ligands are thus much more appropriate for such a purpose, as previously demonstrated in the cyclopentadienyl series.[2,3] The first target which comes to mind is the corresponding η^5 species **6** (Scheme 3), incorporating a biomolecule (B) on the pyrrolyl ring. As mentioned above, such a complex has been synthesized just once in the tetramethyl-substituted form **5** (Scheme 2), which forbids any extra substitution or link with a biomolecule. Furthermore, the presence of both the nitrogen atom and the substituent B on the ring introduces planar chirality and an exciting challenge in separating the resulting enantio- or diastereomers. On the other hand, the tetracarbonyl η^1 complex **7**, built on a strong bidentate pyrrolyl group, offers more possibilities for the attachment of the biomolecule part on the ring as well as on the chelating arm (Scheme 3). This type of ligand was used once, in a pyrrolylthione form for the synthesis of an inorganic species of rhenium.[11]

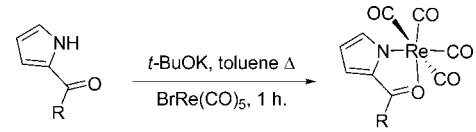
In this preliminary study, we will focus on obtaining simple η^5 or bidentate pyrrolyl organometallic compounds, while the tethering of a biomolecule will be the subject of future research.

The η^5 complexation mode (compound **6** in Scheme 3) was first investigated in this study. Thus, pyrrole and simple mono- or dicoordinating alkyl- or phenyl-substituted pyrroles were reacted according to the reaction conditions encountered in the cyclopentadienyl series, with dirhenium decacarbonyl under neutral conditions[12] or bromorhenium pentacarbonyl and its derivatives ($BrRe(CO)_3(CH_3CN)_2$, $[BrRe(CO)_3(THF)]_2$) under basic conditions.[13] Despite great effort and a thorough screening of reaction conditions (nature of the solvents and bases, modification of concentrations and temperatures), we were not able to isolate any desired products. The reason for this failure could be explained by a poorer σ-donor character of the pyrrolyl ring compared to that of the cyclopentadienyl ring which was studied in the manganese series.[14] It was thus shown[15] that in comparison with the cyclopentadienyltricarbonylmanganese compounds, the higher ν(CO) frequencies encountered in the corresponding pyrrolyl species reflected a greater instability of the metal−CO bond as well as the metal−pyrrolyl bond in these molecules. To overcome this lack of electron density on the metal, the pyrrole **9** containing a dimethylphenylsilyl donor substituent was synthesized in two steps from the N-Boc pyrrole

Scheme 4. Toward the η^5 Coordination Mode



Scheme 5. Synthesis of Bidentate 2-Substituted Pyrrolyltetracarbonylrhenium Complexes



11a R = CCl_3 **12a** (43%)
11b R = OMe **12b** (54%)
11c R = H **12c** (75%)
11d R = Me **12d** (73%)

8 in 46% yield (Scheme 4), according to a procedure reported in the literature for the trimethylsilyl-substituted pyrrole.[16]

This compound was deprotonated in the presence of potassium hydride, and the resulting salt was reacted with bromorhenium pentacarbonyl in refluxing toluene (Scheme 4) for 30 min. The ^{1}H NMR spectra of the crude reaction mixture showed the presence of a new compound, characterized by a pronounced magnetic shielding of its pyrrolyl protons (dd at 5.94, 4.92, and 4.60 ppm in C_6D_6; see the Supporting Information) in comparison with the free corresponding pyrrole (ddd at 6.64, 6.54, and 6.39 ppm in C_6D_6) and consistent with an η^5 coordination mode with loss of the double -bond character in the ring, as encountered in the manganese series.[17] Unfortunately, any atempts to isolate this supposed complex **10** were unsuccessful.

For the study concerning the bidentate pyrrolyl ligands (compound **7** in Scheme 3), the four monosubstituted commercially available pyrroles **11a**−**d** were reacted in refluxing toluene for 1 h in the presence of bromorhenium pentacarbonyl and potassium *tert*-butoxide to give the corresponding complexes **12a**−**d** in medium to good yields (43−75%) (Scheme 5). In contrast to the ^{1}H NMR spectra of compound **10**, these derivatives show a pronounced magnetic deshielding of the pyrrolyl protons in comparison with the case for the free corresponding pyrrole ligands, reflecting the lower π-electron density of the aromatic ring and consistent with an η^1 coordination mode (see the Experimental Section). The four carbonyl stretches of these complexes in the IR spectra, ranging from 1943 to 2012 cm^{-1}, are consistent with C_{2v} symmetry.

These compounds may be placed in the order R = $CCl_3 \approx$ OMe < H, Me in terms of increasing stability. The trichloroacetyl derivative **12a**, in particular, was not fully characterized due to its fast decomposition (see the Experimental Section). This can be attributed to the strong electron-withdrawing effect of the chlorine atoms, which weakens the corresponding

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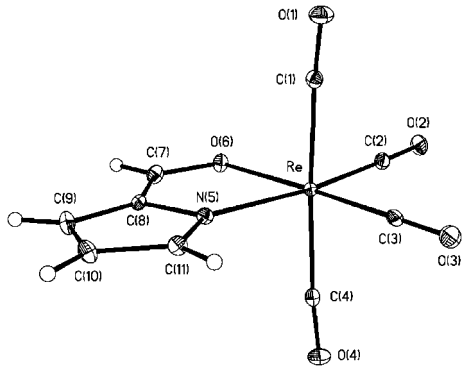
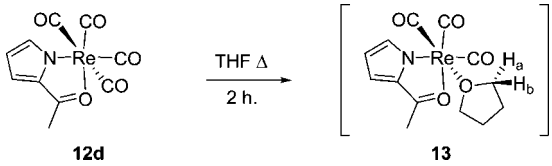
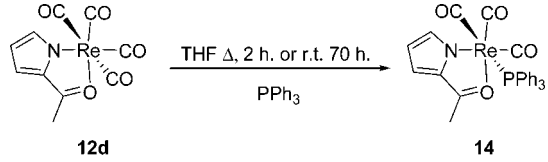


Figure 1. Molecular structure of **12c**. Selected bond lengths (Å) and angles (deg): Re−C(1) = 2.005(5), Re−C(2) = 1.950(5), Re−C(3) = 1.917(5), Re−C(4) = 2.020(5); O(6)−Re−N(5) = 75.96, C(2)−Re−C(3) = 91.65, C(1)−Re−C(2) = 90.26, C(1)−Re−C(3) = 86.74, C(3)−Re−C(4) = 87.52, C(2)−Re−C(4) = 91.52.

Scheme 6. Transformation of 12c in Refluxing THF



Scheme 7. Substitution of One Carbonyl Group in 12d by Triphenylphosphine



oxygen−rhenium link. On the other hand, the relative instability of the more donating methoxy group in compound **12b** could be the result of a greater cis labilization of one carbonyl group.

Crystals of compound **12c** were grown in pentane at low temperature (−15 °C), and its structure was confirmed by an X-ray diffraction study (Figure 1). The average rhenium−carbonyl bond length for the terminal carbonyl groups trans to the pyrrolyl bidentate ligand (1.93 Å) is shorter than the average rhenium−carbonyl bond length in the cis position (2.01 Å). This is in accordance with the mutual trans influence of these latter carbonyl groups and their greater lability under substitution conditions in the presence of L type ligands, as previously reported in the literature for other tetracarbonylrhenium complexes.[18]

Refluxing compound **12d** in THF for 2 h gave the new complex **13** (Scheme 6). The position of the THF ligand was ascribed on the basis of the ^{1}H NMR spectrum of the crude reaction mixture, which shows, for this substitution, a diastereotopic relationship of the CH_2O protons (H_a and H_b as two sets of signals at 3.69 and 3.48 ppm in $CDCl_3$; see the Supporting Information). Such a relationship does not exist in the complexes arising from the substitution of the carbonyl groups trans to the pyrrolyl unit, where the metal is no longer a stereogenic center.

This cis substitution was confirmed by a treatment of compound **12d** with triphenylphosphine in refluxing THF for 30 min or at room temperature for 70 h, which gave the complex **14** in quantitative yield (Scheme 7). The fac configuration of this species was assigned, in the ^{13}C NMR, from the existence

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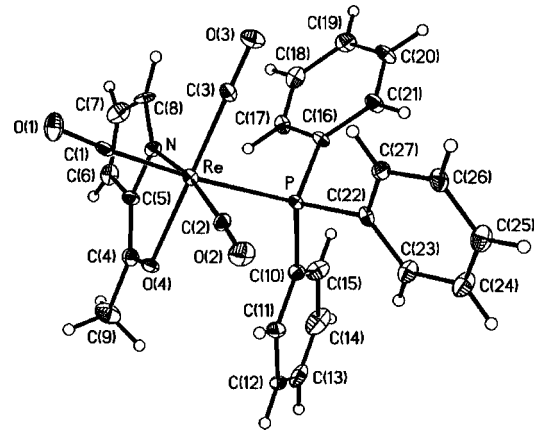
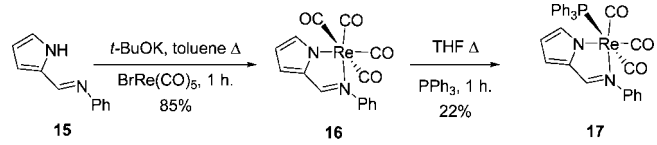


Figure 2. Molecular structure of **14**. Selected bond lengths (Å) and angles (deg): Re−C(1) = 1.955(9), Re−C(2) = 1.941(8), Re−C(3) = 1.904(9), Re−P = 2.496(2); O(4)−Re−N = 75.1, C(2)−Re−C(3) = 92.2, C(1)−Re−C(2) = 91.5, C(1)−Re−C(3) = 88.4, N−Re−P = 90.5, O(4)−Re−P = 89.70.

Scheme 8. Synthesis of Tetracarbonyl- and Tricarbonylrhenium Compounds from the Substituted Pyrrole 15



of a doublet (J_{C-P} = 28.5 Hz) for the CO anti to the phosphine and confirmed by an X-ray diffraction study (Figure 2).

As previously mentioned, the binding arm in our model (Scheme 3) could include the bioligand through its attachment to the L atom. To test this idea, the imine **15** was reacted with bromorhenium pentacarbonyl under the same reaction conditions as for the corresponding pyrrole carboxaldehyde **11c** (Scheme 8). Complex **16** was thus isolated in 85% yield and fully characterized. This compound reacted with triphenylphosphine at THF reflux for 1 h to give **17** in 22% yield, which presents once again a cis substitution of one carbonyl by the phosphine group.

We have studied in this work the access to tricarbonyl- or tetracarbonylrhenium complexes bearing 2-substituted pyrrolyl ligands. We have shown that the η^5 coordination mode of the pyrrolyl ring was not easy to reach, since only one example of such a product type incorporating a silyl substituent was detected in the crude reaction mixture without being isolated. On the other hand, and despite the low affinity of a low-valent rhenium metal center for hard nitrogen and oxygen donor ligands, we have synthesized a series of stable bidentate O,N and N,N pyrrolyl complexes. Most of them are stable enough to be flash chromatographed and kept neat at room temperature for at least 1 month without noticeable decomposition. Their reactivity toward substitution was studied and showed that these species easily lose one carbonyl ligand in the presence of triphenylphosphine or in a coordinating solvent like THF to give the corresponding tricarbonyl compounds, even at room temperature. In addition to the synthesis of potential radiopharmaceuticals, which is currently under investigation with the incorporation of the B part, this CO lability is very promising in the new field of CO-releasing molecules.[19]

Experimental Section Reactions were carried out under argon. Toluene and THF were distilled over sodium benzophenone ketyl. Pyrroles and $BrRe(CO)_5$ were purchased from Aldrich and used as received. Pyrrol-2-ylmethyleneaniline was

synthesized by condensation of aniline on pyrrolecarboxaldehyde in refluxing toluene in the presence of molecular sieves. Thin-layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merck Gerudan SI 60 Å silica gel (35−70 μm) was used for column chromatography. Chromatography solvents were used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 20 °C at 300, 75, and 121.5 MHz, respectively, on a Bruker AVANCE300 spectrometer. Chemical shifts (δ) are given in ppm, referenced to the residual proton resonance of the solvents (7.26 ppm for $CDCl_3$; 7.16 ppm for C_6D_6) or to the residual carbon resonance of the solvent (77.16 ppm for $CDCl_3$; 128.06 ppm for C_6D_6). Melting points (Kofler hot stage) are uncorrected. Elemental analyses were performed by the ICSN.

General Procedure for the Synthesis of the Tetracarbonyl Complexes 12a−d and 16. A solution of $BrRe(CO)_5$ (1 equiv), *t*-BuOK (1.1 equiv), and the appropriate pyrrole (1 equiv) in toluene (8×10^{-2} M) was heated at reflux and stirred for 1 h. The reaction mixture was then cooled to room temperature and purified by flash chromatography using the appropriate eluting system.

{2-(CCl_3CO)-C_4H_3N}$Re(CO)_4$ (12a): 43% yield, pentane/ether 5/5, yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.68 (dd, J = 0.9, 4.6 Hz, 1H), 7.58 (dd, J = 1.2, 1.2 Hz, 1H), 6.56 (dd, J = 1.3, 4.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 188.9, 188.7, 183.7, 181.3, 149.7, 136.1, 128.3, 120, 9.

{2-(CH_3OCO)-C_4H_3N}$Re(CO)_4$ (12b): 53% yield, CH_2Cl_2, yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.12 (dd, J = 1.5, 1.5 Hz, 1H), 6.95 (dd, J = 0.9, 3.9 Hz, 1H), 6.29 (dd, J = 1.5, 3.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 187.5, 187.1, 173.3, 182.9, 138.7, 125.6, 116.7, 113.3, 52.2.

{2-(CHO)-C_4H_3N}$Re(CO)_4$ (12c): 75% yield, pentane/CH_2Cl_2 9/1, yellow crystalline solid, mp 72 °C. ^{1}H NMR ($CDCl_3$): δ 8.73 (d, J = 0.6 Hz, 1H), 7.49 (dd, J = 1.7, 0.9 Hz, 1H), 7.30 (dd, J = 3.2, 0.6 Hz, 1H), 6.51 (dd, J = 3.2, 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 189.1, 184.4, 181.9, 147.3, 145.0, 125.5, 119.2. IR ($CDCl_3$): 2112, 2012, 1991, 1943, 1571 cm^{-1}. Anal. Calcd for $C_9H_4NO_5Re$: C, 27.55; H, 1.03. Found: C, 27.91; H, 1.06.

{2-(CH_3CO)-C_4H_3N}$Re(CO)_4$ (12d): 73% yield, pentane/CH_2Cl_2 9/1, yellow crystalline solid, mp 88 °C. ^{1}H NMR ($CDCl_3$): δ 7.39 (br s, 1H), 7.18 (dd, J = 0.9, 1.2 Hz, 1H), 6.43 (dd, J = 1.5, 4.2 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 193.7, 189.4, 189.2, 184.4, 144.9, 142.8, 123.6, 117.2, 21.8. IR (KBr): 2106, 1989, 1912, 1545 cm^{-1}. Anal. Calcd for $C_{10}H_6NO_5Re$: C, 29.56; H, 1.49. Found: C, 29.50; H, 1.14.

{2-(CHNPh)-C_4H_3N}$Re(CO)_4$ (16): 81% yield, pentane/CH_2Cl_2 8/2, yellow solid, mp 90 °C. ^{1}H NMR ($CDCl_3$): δ 8.06 (d, J = 0.9 Hz, 1H), 7.5−7.3 (m, 2H), 7.3−7.2 (m, 4H), 7.06 (dd, J = 1.0, 3.9 Hz, 1H), 6.42 (dd, J = 1.7, 3.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 189.5, 189.2, 183.9, 160.8, 152.6, 143.9, 141.8, 129.5, 126.6, 122.5, 120.9, 11.6. IR (KBr): 2108, 2002, 1981, 1566 cm^{-1}.

General Procedure for Carbonyl Exchange. A solution of the appropriate complex (1 equiv) with triphenylphosphine (1.1 equiv) in dry THF (1.65×10^{-2} M) was heated to reflux and stirred for 2 h. The reaction mixture was then cooled to room temperature and purified by flash chromatography using an appropriate eluting system.

{2-(CH_3CO)-C_4H_3N}$Re(PPh_3)(CO)_3$ (14): 95% yield, petroleum ether/CH_2Cl_2 95/5, yellow solid, mp 164 °C. ^{1}H NMR ($CDCl_3$): δ 7.4−7.2 (m, 9H), 7.2−7.1 (m, 7H), 6.81 (d, J = 4.1 Hz, 1H), 6.25 (dd, J = 1.3, 4.1 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 194.5 (d, 1C, J = 55.5 Hz), 189.4, 187.2, 186.2, 141.8, 140.5, 131.9, 131.7, 128.4, 128 (d, 3C, J = 42.8 Hz), 126.6, 126.5, 120.2, 114.5, 19.5. ^{31}P NMR ($CDCl_3$): δ 20.31. IR (KBr): 2022, 1923, 1892 cm^{-1}. Anal. Calcd for $C_{27}H_{21}NO_4PRe$: C, 50.62; H, 3.30. Found: C, 50.76; H, 3.41.

{2-(CHNPh)-C_4H_3N}$Re(CO)_4$ (17): 99% yield, petroleum ether/CH_2Cl_2 6/4, orange crystalline solid, mp 166 °C. ^{1}H NMR ($CDCl_3$): δ 7.66 (dd, J = 0.9, 1.9 Hz, 1H), 7.3−7.2 (m, 5H), 7.2−7.1 (m, 7H), 7.0−6.9 (m, 9H), 6.77 (ddd, J = 0.9, 1.7, 3.7 Hz, 1H), 6.21 (dd, J = 1.5, 3.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 196.4 (d, 1C, J = 24 Hz), 188.8, 187.9, 159.2, 152.4, 143.6, 140.6, 133.6, 133.4, 130.6 (d, 3C, J = 42 Hz), 129.9, 128.9, 128.2, 128.1, 125.6, 123.1, 119.9, 115.1. ^{31}P NMR ($CDCl_3$): δ 15.3. IR (KBr): 2019, 1919, 1567 cm^{-1}. Anal. Calcd for $C_{32}H_{24}N_2O_3Pre$: C, 54.77; H, 3.45. Found: C, 54.45; H, 3.18.

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Supporting Information Available: Figures giving NMR spectra of the crude reaction mixture containing compounds **10** and **13** and CIF files giving crystal data for **12c** and **14**.This material is available free of charge via the Internet at http://pubs.acs.org.

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