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Electron Donor-Acceptor Properties of Substituted Pyridine Ligands on *fac*-tricarbonylrhenium(I) Systems.

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Abstract. A series of 4-substituted pyridines were combined with Re(CO)₅Cl to prepare *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes. The Re(I) complexes were characterized by ¹H and ¹³C NMR spectroscopy, FTIR spectroscopy, HRMS, and in the case of L = 4-(trifluoromethyl)pyridine, 4-bromopyridine, 4-picoline, and 4-methoxypyridine, single crystal X-ray diffraction studies. In the carbonyl region of the FTIR spectra for these complexes, the three observed stretches shifted to higher energy as the substituent on the pyridine became more electron withdrawing.

Keywords. Back-bonding, rhenium(I)

1. Introduction

Fac-tricarbonylchlorobis(ligand)rhenium(I) complexes have been studied since the 1950s for their ease of preparation and utility across several fields of chemistry.[1-4] Re(I) complexes are generally air-stable, diamagnetic, (which makes them easy to characterize by ^1H and ^{13}C NMR), have strong CO absorptions in IR spectroscopy, and often are emissive in solution.[5-7] These features have led to researchers increasingly finding utility for rhenium in biological systems as a probe and spectroscopic tool.[8-12] Related rhenium complexes have been studied for their catalytic reduction of CO_2 to CO.[13-16] *Fac*-tricarbonylrhenium(I) complexes serve as cold analogs for radioactive $^{99\text{m}}\text{Tc(I)}$ biological imaging agents, and more recently, with the availability of ^{188}Re complexes, there is interest in using rhenium for therapeutic agents.[17-19] Generally prepared from the $\text{Re}(\text{CO})_5\text{Cl}$ starting material, the strong *trans* directing influence of the CO ligands results in the facile substitution of two equivalents of CO that are *cis* to one another. The ability to reliably control the stereochemistry of these complexes has resulted in numerous reports of well-defined organometallic macrocycles.[20,21]

Carbon monoxide is a classic ligand in inorganic chemistry for describing back-bonding. In back-bonding, electron density from filled nonbonding d-orbitals of the appropriate symmetry donate electron density into the LUMO of a carbon monoxide ligand, which happens to be π^* anti-bonding in character. The result of this interaction is the strengthening of the metal-carbonyl bond at the expense of the internal carbon-oxygen triple bond of the carbon monoxide. For this study, we compared the known $\text{Re}(\text{CO})_3(\text{pyridine})_2\text{Cl}$ complex with five new complexes where electron donating and withdrawing substituents have been attached in the 4-position of the pyridine. Looking at FTIR spectroscopy and single crystal X-ray diffraction studies, we were able to show that these electronic differences are easily shown by FTIR spectroscopy, but too subtle to be picked up by examining the bond lengths in X-ray structures.

2. Materials and Methods

2.1 Materials

The chemicals $\text{Re}(\text{CO})_5\text{Cl}$, pyridine, 4-(trifluoromethyl)pyridine, 4-bromopyridine·HCl, 4-picoline, 4-acetylpyridine, and 4-methoxypyridine were purchased from commercial sources and used as received.

2.2 Instrumentation

NMR spectra were recorded on an Oxford AS400 spectrometer and referenced to residual peaks in the deuterated solvents. IR data was collected on a PerkinElmer Spectrum One FT-IR Spectrometer with a liquid cell with KBr windows.

X-ray intensity data for compounds **1a**, **1b**, and **1d** were measured at 100 K on a Bruker APEX I CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (Mo K α radiation, $\lambda = 0.71073$ Å) operated at 2000 W power. X-ray intensity data for **1f** were measured on a Bruker APEX II CCD-based diffractometer with dual Cu/Mo I μ S microfocus optics (Mo K α radiation, $\lambda = 0.71073$ Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a stream of nitrogen at 100 K (Oxford Cryosystems). The detector was placed at a distance of 5.9 cm for **1a**, **1b** and **1d** and 4.00 cm for **1f** from the crystal. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of F² converged.

2.3 Typical Reaction for synthesis of Re(CO)₃(L)₂Cl

One equivalent (0.100 g, 0.276 moles) of Re(CO)₅Cl and 2.2 equivalents (0.608 moles) of a 4-substituted pyridine derivative (R = OMe, CH₃, H, CF₃, COCH₃) were added to a 25 mL round bottom flask followed by 10.0 mL of 95% ethanol and a magnetic stir bar. The solution was refluxed for one hour under a N₂ atmosphere. Pyridine generally required longer reflux times (overnight) to fully react. The solution was removed from heat, the solvent evaporated *in vacuo*, and the final product was isolated using an overnight dual-solvent recrystallization. If any powder was generated during the reflux (as in the case of trifluoromethylpyridine) the powder was first removed using vacuum filtration before recrystallization.

Procedure for the 4-bromopyridine derivative:

The compound 4-bromopyridine was purchased as an HCl salt, so 0.177 g (1 equivalent, 0.912 mmol) of bromopyridine·HCl and 0.106 g (1.1 equivalents, 1.00 moles) of Na₂CO₃ were combined in a 50 mL flask. Approximately 10 mL of distilled water were added and the solution was mixed well. The solution was transferred to a separatory funnel and washed twice with five mL

portions of ether. The organic layer was isolated, dried with magnesium sulfate, and filtered via vacuum filtration. The solvent was removed *in vacuo*, in a tared 25 mL round bottom flask. The amount of 4-bromopyridine isolated was calculated, and then 0.45 equivalents of $\text{Re}(\text{CO})_5\text{Cl}$ was added to the round bottom along with a stir bar. The solution was refluxed in 10.0 mL of 95% ethanol for one hour, and then the solvent was removed *in vacuo*. Clean product was isolated from a dual solvent recrystallization from dichloromethane/ether.

2.4 Characterization

1a. *fac*- $\text{Re}(\text{CO})_3(4\text{-MeOPy})_2\text{Cl}$: ^1H NMR (CDCl_3) δ 8.53 (d, 2H, $J = 3.4$ Hz), 6.80 (d, 2H, $J = 3.4$ Hz), 3.88 (s, 3H); ^{13}C NMR (CDCl_3) δ 195.83, 192.90, 167.05, 154.68, 111.75, 56.07; FTIR (CHCl_3): $\nu_{\text{CO}} = 2024, 1917, 1885\text{ cm}^{-1}$; HRMS (ESI^+) $[\text{M}-\text{Cl}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_5\text{Re}$ 489.0461, found 489.0464; yield = 10%; Recrystallized from $\text{CHCl}_3/\text{Et}_2\text{O}$.

1b. *fac*- $\text{Re}(\text{CO})_3(4\text{-MePy})_2\text{Cl}$: ^1H NMR (CDCl_3) δ 8.58 (d, 2H, $J = 6.4$ Hz), 7.13 (d, 2H, $J = 6.4$ Hz), 2.39 (s, 3H); ^{13}C NMR (CDCl_3) δ 195.70, 192.71, 152.99, 150.88, 126.59, 21.27; FTIR (CHCl_3): $\nu_{\text{CO}} = 2025, 1920, 1886\text{ cm}^{-1}$; HRMS (ESI^+) $[\text{M}-\text{Cl}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3\text{Re}$ 457.0562, found 457.0571; yield = 69%; Recrystallized from $\text{CH}_2\text{Cl}_2/\text{pentane}$.

1c. *fac*- $\text{Re}(\text{CO})_3(\text{Py})_2\text{Cl}$: Known Compound[1]. FTIR (CHCl_3): $\nu_{\text{CO}} = 2027, 1923, 1889\text{ cm}^{-1}$; yield = 24%; Recrystallized from $\text{CH}_2\text{Cl}_2/\text{pentane}$.

1d. *fac*- $\text{Re}(\text{CO})_3(4\text{-BrPy})_2\text{Cl}$: ^1H NMR ($\text{d}^6\text{-DMSO}$) δ 8.60 (d, 2H, $J = 1.2$ Hz), 7.43 (d, 2H, $J = 1.2$ Hz); ^{13}C NMR ($\text{d}^6\text{-DMSO}$) δ 195.68, 191.54, 154.16, 136.04, 129.57; FTIR (CHCl_3): $\nu_{\text{CO}} = 2027, 1927, 1891\text{ cm}^{-1}$; HRMS (ESI^+) $[\text{M}-\text{Cl}]^+$ Calcd for $\text{C}_{13}\text{H}_8\text{Br}_2\text{N}_2\text{O}_3\text{Re}$ 584.8459, found 584.8447; yield = 23%; Recrystallized from $\text{CH}_2\text{Cl}_2/\text{pentane}$.

1e. *fac*- $\text{Re}(\text{CO})_3(4\text{-C}(\text{O})\text{CH}_3\text{Py})_2\text{Cl}$: ^1H NMR (CDCl_3) δ 8.98 (dd, 2H, $J = 5.2, 1.6$ Hz), 7.77 (dd, 2H, $J = 5.2, 1.6$ Hz), 2.65 (s, 3H); ^{13}C NMR (CDCl_3) δ 194.89, 191.96, 155.06, 144.15, 123.58, 26.87; FTIR (CHCl_3): $\nu_{\text{CO}} = 2029, 1928, 1893\text{ cm}^{-1}$; HRMS (ESI^+) $[\text{M}-\text{Cl}]^+$ Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_3\text{Re}$ 513.0460, found 513.0456; yield = 87%; Recrystallized from $\text{CHCl}_3/\text{Et}_2\text{O}$.

1f. *fac*- $\text{Re}(\text{CO})_3(4\text{-CF}_3\text{Py})_2\text{Cl}$: ^1H NMR ($\text{d}^6\text{-DMSO}$) δ 9.04 (d, 2H, $J = 6.4$ Hz), 7.63 (d, 2H, $J = 6.4$ Hz); ^{13}C NMR ($\text{d}^6\text{-DMSO}$) δ 195.51, 191.31, 155.07(m), 140.70(q, $J = 35.6$ Hz), 122.10 (m), 121.95 (q, $J = 72.5$ Hz); FTIR (CHCl_3): $\nu_{\text{CO}} = 2029, 1928, 1893\text{ cm}^{-1}$; HRMS (ESI^+) $[\text{M}-\text{Cl}]^+$ Calcd for $\text{C}_{15}\text{H}_8\text{F}_6\text{N}_2\text{O}_3\text{Re}$ 564.9997, found 564.9994; yield = 87%; Recrystallized from $\text{CH}_2\text{Cl}_2/\text{pentane}$.

3. Results and Discussion

Five new Re(I) compounds (**1a**, **1b**, **1d-f**) and one known compound[1] (**1c**) were synthesized by combining one equivalent of $\text{Re}(\text{CO})_5\text{Cl}$ and 2.2 equivalents of a 4-substituted pyridine derivative in refluxing ethanol for an hour, Figure 1. The solvent methanol also works, but the reflux time must be extended, presumably to compensate for its lower boiling point. In the case of 4-bromopyridine, the ligand is only available as the HCl salt, and must be deprotonated before the reaction with Re(I) can take place. After the reflux was finished, the ethanol was removed *in vacuo*, and clean product was generally obtained using a dual solvent recrystallization system. Yields ranged from 10 to 87%. Although some of these values are low, in all cases pure samples suitable for characterization were obtained. The resulting product was the *fac*- $\text{Re}(\text{CO})_3(\text{L})_2\text{Cl}$. The *fac* product is a result of the strong *trans* directing nature of the CO ligands, that labilizes two equivalents of CO. Many groups have taken advantage of this reactivity to build molecular architectures such as squares[4,21-23] and rectangles[24-28] because the two new ligands are forced into a *cis* arrangement in this family of structures.

The structures of complexes **1a-f** were confirmed by a variety of analytical techniques. ^1H and ^{13}C NMR showed in all cases that the pyridine derivatives were in a single type of environment, consistent with the proposed structures. Upon binding to the Re(I), the ^1H NMR peaks of the pyridine derivatives would general shift slightly downfield, consistent with previous observations.[2] Most ^1H NMR samples were measured in CDCl_3 , but solubility issues led to the use of d^6 -DMSO for the CF_3 derivative **1f**. For all of these complexes, there are two peaks in the ^{13}C spectra from the CO ligands. One peak corresponds to the two CO ligands *trans*- to the pyridine derivative, and one peak is from the CO *trans* to the chloride ligand. In both cases, these CO peaks are difficult to detect and of low intensity, as is commonly the case in ^{13}C NMR when a C atom lacks C-H bonds.

The point group of these *fac*- $\text{Re}(\text{CO})_3(\text{L})_2\text{Cl}$ complexes are all C_s , and as such one would expect three carbonyl stretches in the FTIR spectra. All six compounds **1a-f** exhibited the predicted three stretches when dissolved in CHCl_3 and measured in liquid sample cells. For the underivatized pyridine complex (**1c**), these three stretches occur at $\nu = 2027, 1923, \text{ and } 1889 \text{ cm}^{-1}$, respectively, Table 1. To compare the electronic effects of various substituents, we have used the σ_{para} Hammett Constant, which measures how electron donating or withdrawing a chemical group is when placed in the *para* position of an aromatic ring.[29] For this study, the

methoxy and methyl groups were electron donating (and had negative values for their σ_{para}), and the bromo, acetyl, and trifluoromethyl groups were electron withdrawing (and had positive values for their σ_{para}). Ligands with electron donating groups, would be expected to donate more electron density to the metal through their metal-ligand bonds. This extra electron density at the metal center, should then result in stronger back bonding, where the filled non-bonding d-orbitals donate electron density into ligand (in this case CO) orbitals with the appropriate symmetry. In these *fac*-Re(CO)₃(L)₂Cl complexes, the LUMO of the CO that accepts the back bonding is a π^* orbital. One would therefore expect, that as the ligands become more electron donating, that because of back bonding, the bond between the Re(I) and the CO should strengthen, and the bond between the C and O within the CO should weaken (because they have a more strongly populated π^* LUMO). This trend is in fact observed, as shown in Table 1, where the FTIR stretches for COs in the *fac*-Re(CO)₃(L)₂Cl complex with the most electron donating group (-OMe), have the lowest energy. For all of the measured CO stretches in this study, the CO bond strengthens as you put stronger electron withdrawing groups on the para position of the pyridine ligands.

Although the trends in back bonding are clearly observable by looking at the FTIR spectra of the carbonyl peaks, no reliable patterns were observed in the single crystal X-ray diffraction studies of these complexes. The crystal structure of the pyridine derivative **1c** has previously been reported,[30] and four new crystal structures were obtained for this study. Single crystals of **1a**, **1b**, **1d**, and **1f** were grown by dual solvent recrystallizations as detailed in the experimental section. All of the solid state structures were consistent with the proposed *fac*-Re(CO)₃(L)₂Cl geometries. Selected bond lengths (Å) are reported in Table 3. No consistent trends are observed when one compares the C≡O, the C-Re, or the Re-N bond lengths in light of the σ_{para} Hammett constant. One would expect, judging by the FTIR data as one examines the bond lengths of **1a** through **1f**, that the C≡O bonds would decrease in length (higher energy stretches correspond to stronger bonds). Simultaneously, the Re-C bonds should increase in length (greater backbonding puts more electron density into the π^* antibonding orbital, corresponding to a shorter C≡O bond). In some cases, this is an issue of resolution, where the average bond lengths ranges overlap with one another when taking the error bars into account. It is possible that solid-state packing effects could also contribute to the lack of trend.

4. Conclusion

We have synthesized and characterized five new and one previously known *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes where the ligand is pyridine and five derivatives of pyridine substituted at the 4-position. These derivatives consist of one that is electron donating through resonance (OMe), one that is electron donating inductively (-Me), one that is electron withdrawing by resonance (-C(O)Me), one that is electron withdrawing inductively (-CF₃), and finally, one that is electron withdrawing inductively and electron donating by resonance (-Br). All six of these complexes can be prepared and result in air-stable products. The Re(I) complexes are diamagnetic and are thus easily characterizable by ¹H and ¹³C NMR. Four of the five new complexes have their solid state structures determined by single crystal X-ray diffraction studies. The electronic effects of the ligands is measurable using FTIR and confirms known trends in back bonding, but is too subtle to be noticed in the bond lengths obtained from the single crystal X-ray diffraction studies.

Appendix A. Supplementary material

The following are the supplementary material related to this article: CCDC 1450312 (for **1a**), 1450313 (for **1b**), 1450314 (for **1d**), and 1450315 (for **1f**) contain the supplementary crystallographic data for this paper. These material can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Artwork.

Figure 1. Synthetic scheme for synthesis of **1a-f**.

Figure 2. ORTEP drawing of **1a**, **1b**, **1d**, and **1f** with solvent and hydrogen atoms omitted for clarity. See Table 3 for select bond distances and angles.

Table 1. σ_{para} Hammett Constants[29] for ligands and CO stretches (cm^{-1}) of $[\text{Re}(\text{CO})_3\text{Cl}(\text{Ligand})_2]$ complexes measured in CHCl_3 solutions using FTIR.

Re(I) Complex	σ_{para} Hammett Constant of 4- substituent on pyridine ligand	FTIR of CO stretches (cm^{-1})		
1a	-0.27	2024	1917	1885
1b	-0.17	2025	1920	1886
1c	0	2027	1923	1886
1d	0.23	2029	1927	1891
1e	0.50	2029	1928	1893
1f	0.54	2032	1933	1897

Table 2Crystallographic data for complexes **1a**, **1b**, **1d**, and **1f**

Compound	1a	1b	1d	1f
Formula	C ₁₅ H ₁₄ ClN ₂ O ₅ Re	C ₁₅ H ₁₄ ClN ₂ O ₃ Re	C ₁₃ H ₈ Br ₂ ClN ₂ O ₃ Re	C ₁₅ H ₈ ClF ₆ N ₂ O ₃ Re
Fw	523.93	791.93	621.68	599.88
T/K	100(2)	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	C2/c	C2/c	P2(1)/c
Crystal size /mm	0.21x0.18x0.13	0.37x0.15x0.13	0.03x0.02x0.01	0.39x0.36x0.23
a/Å	12.8621(15)	23.435(11)	16.3901(14)	13.1897(9)
b/ Å	10.0587(12)	10.994(5)	12.1582(14)	6.8212(5)
c/ Å	13.5289(15)	14.136(6)	20.471(2)	20.6827(14)
α/°	90	90	90	90
β/°	105.1040(10)	90.228(5)	95.987(2)	102.187(3)
γ/°	90	90	90	90
V/ Å ³	1689.8(3)	3642(3)	4057.2(7)	1818.9(2)
Z	4	8	8	4
D _{calcd} /g cm ⁻³	2.059	1.794	2.036	2.191
μ/mm ⁻¹	7.376	6.831	10.070	6.906
F(000)	1000	1872	2288	1128
θ _{max} /°	1.64 to 26.38	1.74 to 25.11	2.00 to 25.03	1.68 to 25.06
Collected	13188	12583	14424	52090
Unique reflns	3457	3200	3598	3218
	[R(int)=0.0414]	[R(int)=0.0440]	[R(int)=0.0386]	[R(int)=0.0426]
Coverage of independent reflns	100%	98.4%	99.9	99.9
Data/restraints/parameters	3457/0/219	3200/0/201	3598/1/202	3218/0/253
GOF	1.027	1.028	1.033	0.973
Final R indices [<i>I</i> > 2.0σ(<i>I</i>)]	R1=0.0268, wR2=0.0583	R1=0.0201, wR2=0.0508	R1=0.0249, wR2=0.0628	R1=0.0197, wR2=0.0867
R indices (all data)	R1=0.0333, wR2=0.0614	R1=0.0214, wR2=0.0514	R1=0.0277, wR2=0.0642	R1=0.0235, wR2=0.1067
Largest diff. peak, hole/e Å ⁻³	2.033 and - 0.856	1.161 and - 0.925	1.201 and -0.815	1.186 and -1.250

Table 3. Bond Lengths (Å) for Re(I) pyridine complexes

	1a	1b	1c	1d	1f	Relationship
Re-N1	2.210(4)	2.215(3)	2.211(3)	2.202(4)	2.210(3)	<i>Trans</i> to C2
Re-N2	2.212(4)	2.218(2)		2.222(4)	2.220(3)	<i>Trans</i> to C3
Re-C1	1.951(5)	1.910(4)	1.92(1)	1.919(6)	1.917(4)	<i>Trans</i> to Cl
Re-C2	1.913(5)	1.917(3)	1.913(3)	1.912(5)	1.909(4)	<i>Trans</i> to N1
Re-C3	1.900(5)	1.921(3)		1.916(5)	1.910(4)	<i>Trans</i> to N2
Re-Cl	2.471(1)	2.486(1)	2.447(1)	2.484(1)	2.474(1)	<i>Trans</i> to C1
C1-O1	1.076(6)	1.132(4)	1.160(5)	1.119(7)	1.140(5)	<i>Trans</i> to Cl
C2-O2	1.154(6)	1.153(4)	1.18(1)	1.150(6)	1.165(5)	<i>Trans</i> to N1
C3-O3	1.158(7)	1.158(4)		1.168(6)	1.157(4)	<i>Trans</i> to N2

Graphical Abstract

A series of 4-substituted pyridines were combined with $\text{Re(CO)}_5\text{Cl}$ to prepare *fac*-tricarbonylchlorobis(ligand)rhenium(I) complexes. Electronic effects of the substituents were observed in the carbonyl region of the FTIR spectra for these complexes, but not in the X-ray structures.