Complexes Having the *fac*-{M(CO)$_3$}$^+$ Core (M = Tc, Re) Useful in Radiopharmaceuticals. X-ray and NMR Structural Characterization and Density Functional Calculations of Species Containing Two *sp*^{3} N Donors and One *sp*^{3} O Donor

Malgorzata Lipowska,[†] Renzo Cini,[◊] Gabriella Tamasi,[◊] Xiaolong Xu,[†] Andrew T. Taylor,[†] and Luigi G. Marzilli,[*,‡]

Department of Radiology, Emory University, Atlanta, GA 30322, USA
Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA
Department of Chemical and Biosystem Sciences and Technologies, University of Siena, I-53100 Siena, Italy

Supporting Information

Table S-1. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Re(CO)_3(NH_3)_2(H_2O)]^+$ (**3**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	-0.122008	-0.002545	0.012420
O1	-1.637048	0.180364	-1.676547
O5	1.754593	-0.253371	2.452084
O6	1.614661	2.336254	-1.070285
O7	1.644967	-2.027491	-1.548050
N1	-1.527636	-1.628384	0.734267
N2	-1.557188	1.402468	1.062142
C7	1.035758	-0.157292	1.517568
C8	0.954198	1.446799	-0.658528
C9	0.972959	-1.257372	-0.954579
H1OA	-1.721959	-0.554951	-2.315918
H1OB	-1.722045	1.035545	-2.143596
H1NA	-1.114268	-2.556785	0.597638
H1NB	-1.718474	-1.528640	1.736814
H1NC	-2.418588	-1.593302	0.227866
H2NA	-1.754385	1.079354	2.015126
H2NB	-2.443772	1.468876	0.551234
H2NC	-1.156987	2.343334	1.140098

Table S-2. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Tc(CO)_3(NH_3)_2(H_2O)]^+$ (**4**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	Z
Tc1	-0.162399	0.000077	0.014045
O1	-1.667021	0.039633	-1.706096
O5	1.711176	-0.048122	2.469580
O6	1.605414	2.215491	-1.270346
O7	1.593929	-2.174541	-1.352986
N1	-1.567279	-1.558800	0.892562
N2	-1.562826	1.526430	0.951351
C7	0.995847	-0.029720	1.532060
C8	0.936076	1.376681	-0.784044
C9	0.928927	-1.351161	-0.835384
H1OA	-1.760139	-0.747776	-2.277986
H1OB	-1.756798	0.850918	-2.244145
H1NA	-1.161176	-2.495820	0.811902
H1NB	-1.728909	-1.377825	1.887828
H1NC	-2.467853	-1.547863	0.404423
H2NA	-1.772673	1.274390	1.921852
H2NB	-1.129849	2.454809	0.960043
H2NC	-2.441802	1.577975	0.427734

Table S-3. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Re(CO)_3(EN)(H_2O)]^+$ (**5**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	-0.183745	-0.061793	0.024372
O1	0.196409	-2.163934	0.831953
O5	-0.515524	2.807829	-1.061472
O6	-2.385654	0.489722	2.150416
O7	-2.355234	-1.051524	-1.973784
N1	1.575879	-0.493292	-1.324175
N2	1.552556	0.461478	1.339768
C3	2.870327	-0.457048	-0.538601
C4	2.793226	0.668015	0.495896
C7	-0.388208	1.706647	-0.644793
C8	-1.548735	0.280098	1.342332
C9	-1.530716	-0.675722	-1.215082
H1OA	-0.158885	-2.400382	1.711693
H1OB	0.104497	-2.924259	0.224054
H1NA	1.454956	-1.408338	-1.770826
H1NB	1.608972	0.195508	-2.083048
H2NA	1.717749	-0.293587	2.013575
H2NB	1.339801	1.310147	1.874487
H3A	2.990672	-1.426011	-0.041384
H3B	3.728597	-0.308222	-1.203295
H4A	2.704352	1.643665	0.005177
H4B	3.695744	0.679961	1.117115

Table S-4. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Tc(CO)_3(EN)(H_2O)]^+$ (**6**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Tc1	-0.225442	-0.080125	0.031120
O1	0.127797	-2.169396	0.908513
O5	-0.544774	2.762870	-1.126937
O6	-2.424739	0.547329	2.144648
O7	-2.409037	-1.110498	-1.940091
N1	1.532862	-0.544812	-1.316551
N2	1.507283	0.497283	1.336502
C3	2.813808	-0.495341	-0.516197
C4	2.742799	0.663023	0.482178
C7	-0.422627	1.675401	-0.683970
C8	-1.592519	0.309899	1.344884
C9	-1.583735	-0.721063	-1.195060
H1OA	-0.257706	-2.392130	1.778596
H1OB	0.083097	-2.947548	0.318811
H1NA	1.407762	-1.468844	-1.741627
H1NB	1.567117	0.131649	-2.085578
H2NA	1.666990	-0.230020	2.040561
H2NB	1.291845	1.368325	1.831523
H3A	2.915253	-1.448334	0.015841
H3B	3.685087	-0.380094	-1.171286
H4A	3.649991	0.688515	1.096918
H4B	2.663225	1.622610	-0.041665

Table S-5. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $Re(CO)_3$(ENAC), isomer δ-EN (**7a**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	-0.438741	-0.051362	0.049818
O1	1.267482	-0.879159	1.040071
O2	3.436863	-1.617421	0.772855
O5	-2.626590	1.567458	-1.446511
O6	-2.558781	-1.072610	2.078789
O7	-0.998504	-2.519798	-1.755366
N1	1.363951	0.664690	-1.103605
N2	0.234516	1.677757	1.279882
C1	2.400235	-1.065803	0.353303
C2	2.343769	-0.488402	-1.088253
C3	1.968265	1.898552	-0.459714
C4	0.936952	2.658658	0.383835
C7	-1.785092	0.944822	-0.870988
C8	-1.749317	-0.682682	1.304097
C9	-0.784646	-1.576730	-1.065694
H1N	1.087088	0.875840	-2.064975
H2NA	0.881768	1.242964	1.950532
H2NB	-0.532557	2.123088	1.787770
H2A	3.347787	-0.177284	-1.399376
H2B	1.983631	-1.263869	-1.774253
H3A	2.789033	1.563907	0.185264
H3B	2.395947	2.558730	-1.223191
H4A	0.177133	3.130403	-0.250024
H4B	1.441738	3.442981	0.959745

Table S-6. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $Re(CO)_3$(ENAC), isomer λ-EN (**7b**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	-.462378	-.030168	.045755
O1	1.180480	-1.095015	.883953
O2	3.390565	-1.704487	.657243
O5	-2.543376	1.924253	-1.178818
O6	-2.535138	-.958063	2.167927
O7	-1.422226	-2.279347	-1.870069
N1	1.278695	.600711	-1.225246
N2	.511743	1.499314	1.375942
C1	2.346281	-1.161020	.240527
C2	2.333238	-.478512	-1.153013
C3	1.747669	1.951158	-.743759
C4	1.817779	1.978823	.788887
C7	-1.743007	1.172566	-.707837
C8	-1.744066	-.603930	1.357996
C9	-1.055205	-1.419320	-1.137508
H1N	.958851	.694631	-2.191838
H2NA	.689223	.981283	2.242109
H2NB	-.122818	2.276219	1.572071
H2A	2.089356	-1.242864	-1.900018
H2B	3.330705	-.081612	-1.374958
H3A	2.731234	2.191163	-1.164148
H3B	1.026493	2.694588	-1.102849
H4A	2.613129	1.316943	1.150910
H4B	2.050520	2.994768	1.128619

Table S-7. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $Tc(CO)_3$(ENAC), isomer δ-EN (**8a**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Tc1	-0.529812	-0.063563	0.059128
O1	1.183398	-0.889334	1.053450
O2	3.360410	-1.594987	0.764038
O5	-2.752179	1.510308	-1.435676
O6	-2.618717	-1.121691	2.104513
O7	-1.049380	-2.552495	-1.733724
N1	1.261561	0.678249	-1.100301
N2	0.106014	1.680740	1.292359
C1	2.311180	-1.051725	0.358060
C2	2.246755	-0.466385	-1.081240
C3	1.843435	1.911309	-0.442466
C4	0.796852	2.660674	0.391764
C7	-1.900644	0.907254	-0.862918
C8	-1.824198	-0.719230	1.326547
C9	-0.851679	-1.605433	-1.051526
H1N	0.986339	0.891515	-2.061488
H2NA	-0.658441	2.118945	1.809237
H2NB	0.758324	1.232931	1.948240
H2A	3.250127	-0.150258	-1.391132
H2B	1.894946	-1.244592	-1.769243
H3A	2.658191	1.580553	0.212894
H3B	2.277683	2.581308	-1.194299
H4A	0.034411	3.117168	-0.250901
H4B	1.288842	3.459543	0.959636

Table S-8. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $Tc(CO)_3$(ENAC), isomer λ-EN (**8b**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Tc1	-.559131	-.034194	.055119
O1	1.080894	-1.116964	.891743
O2	3.300436	-1.685010	.652305
O5	-2.664213	1.902097	-1.159109
O6	-2.610936	-.989387	2.189336
O7	-1.498787	-2.297840	-1.856020
N1	1.169536	.606795	-1.227201
N2	.403888	1.501208	1.393691
C1	2.242349	-1.156639	.243789
C2	2.221195	-.471040	-1.149726
C3	1.628443	1.953429	-.734588
C4	1.704969	1.973655	.798178
C7	-1.857712	1.160263	-.693913
C8	-1.831013	-.626303	1.378086
C9	-1.140841	-1.435543	-1.128005
H1N	.852086	.702950	-2.194111
H2NA	.581496	.961905	2.245826
H2NB	-.225949	2.277680	1.603584
H2A	3.219383	-.076121	-1.374387
H2B	1.977866	-1.237963	-1.895000
H3A	2.609327	2.206366	-1.154946
H3B	.901351	2.696024	-1.084877
H4A	1.949378	2.987331	1.138086
H4B	2.500225	1.306071	1.151324

Table S-9. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Re(CO)_3(ENDAC)]^-$, isomer A δ-EN –*anticlinal*-CH_2COO^- (**9a**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	-0.627825	-0.423866	-0.036186
O1	-0.492913	1.377539	-1.208242
O2	-1.135820	3.590648	-1.341223
O3	3.869972	-1.140134	0.244657
O4	4.817493	0.617028	-0.964150
O5	-0.744666	-2.793517	1.966298
O6	-0.126492	-2.418824	-2.367175
O7	-3.700469	-0.624200	-0.511135
N1	-0.752854	1.279781	1.431234
N2	1.518275	-0.105883	0.415797
C1	-1.007111	2.502375	-0.731247
C2	-1.494175	2.396377	0.743180
C3	0.641664	1.715016	1.838370
C4	1.608101	0.533951	1.774701
C5	2.417305	0.594940	-0.581087
C6	3.858021	-0.021806	-0.425526
C7	-0.699588	-1.879288	1.193725
C8	-0.318046	-1.656573	-1.476530
C9	-2.522451	-0.547394	-0.329045
H1N	-1.269681	0.968006	2.256337
H2N	2.058920	-1.003200	0.505752
H2A	-1.341970	3.358170	1.245923
H2B	-2.564825	2.162564	0.741373
H3A	0.958879	2.486376	1.127496
H3B	0.621345	2.163607	2.838028
H4A	1.353479	-0.221333	2.526817
H4B	2.635459	0.863140	1.967403
H5A	2.039882	0.422618	-1.595395
H5B	2.438255	1.678793	-0.420501

Table S-10. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Re(CO)_3(ENDAC)]^-$, isomer A λ-EN -*antiperiplanar*-CH_2COO^- (**9b**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	-0.617310	-0.451208	-0.015923
O1	-0.718352	1.264179	-1.297773
O2	-1.382702	3.463112	-1.498193
O3	3.895095	-0.388340	0.985511
O4	4.912170	0.170363	-1.038742
O5	-0.317141	-2.687138	2.118691
O6	-0.009210	-2.503331	-2.268037
O7	-3.660546	-1.057079	-0.271955
N1	-0.904354	1.272135	1.407197
N2	1.490355	0.224830	0.251553
C1	-1.199458	2.409448	-0.841737
C2	-1.589852	2.387817	0.661717
C3	0.445941	1.656429	1.968723
C4	1.502605	1.598689	0.866769
C5	2.485456	0.169676	-0.888689
C6	3.920497	-0.023429	-0.266388
C7	-0.432786	-1.825711	1.296297
C8	-0.241851	-1.718251	-1.406446
C9	-2.492615	-0.824559	-0.173695
H1N	-1.504446	0.960451	2.173349
H2N	2.011427	-0.367317	0.942149
H2A	-1.362135	3.363514	1.105538
H2B	-2.672056	2.224824	0.717255
H3A	0.400644	2.656380	2.414664
H3B	0.691901	0.933517	2.754675
H4A	2.496140	1.792214	1.286596
H4B	1.300890	2.338663	0.084102
H5A	2.262680	-0.691341	-1.528876
H5B	2.429053	1.076159	-1.501816

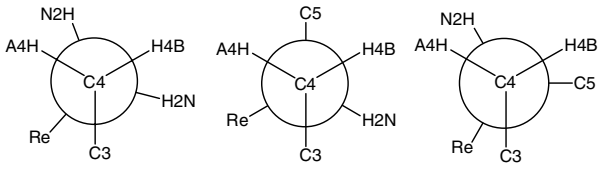
Table S-11. Computed atomic orthogonal coordinates (x·10, y·10, z·10 Å) for $[Re(CO)_3(ENDAC)]^-$, isomer B λ-EN +*antiperiplanar*-CH_2COO^- (**9c**) optimized at the DFT-Becke3LYP/LANL2DZ level.

Atom	x	y	z
Re1	0.583767	-0.471487	0.026316
O1	1.051801	1.226147	1.249490
O2	2.007559	3.324198	1.311194
O3	-5.041727	-0.144957	-0.241265
O4	-3.718132	0.885179	1.384730
O5	-0.220669	-2.664316	-2.018823
O6	0.078341	-2.440919	2.377570
O7	3.551567	-1.398802	-0.132464
N1	0.819487	1.211484	-1.446635
N2	-1.449081	0.440600	0.133724
C1	1.592942	2.306372	0.707266
C2	1.731175	2.245917	-0.839017
C3	-0.557350	1.736543	-1.786566
C4	-1.419759	1.797342	-0.525587
C5	-2.632113	-0.361812	-0.361209
C6	-3.942390	0.181746	0.318391
C7	0.089517	-1.818774	-1.230229
C8	0.271502	-1.688251	1.478979
C9	2.412925	-1.043023	-0.071546
H1N	1.250127	0.840932	-2.295996
H2N	-1.736507	0.634935	1.115408
H2A	1.539872	3.241486	-1.255387
H2B	2.766851	1.968003	-1.065418
H3A	-0.481292	2.726165	-2.251305
H3B	-0.999806	1.044308	-2.511937
H4A	-2.439699	2.115044	-0.770346
H4B	-1.018122	2.520332	0.193505
H5A	-2.494622	-1.410757	-0.074976
H5B	-2.710754	-0.312134	-1.453211

Additional explanations of NMR shifts employing Newman Projection.

The resemblance of the 1D ^{1}H NMR spectra (particularly for the H3 signals) of **1A** and **2** in aqueous solution and their difference from **1B** could be explained by analyzing the Newman projection formulas for all three complexes. In the Newman projection (Chart S1) we look at the C4-N2 bond head on; for clarity, the C3 and C5 methylene protons and other parts of the complexes are omitted; H2N represents N2 amine protons. In **1A**, the C3-C4-N2-C5 torsion angle is *trans* (171º) but in **1B**, the C3-C4-N2-C5 torsion angle is *gauche* (-89º). Consequently, the H3B-H5A distance is much shorter in **1B** (2.4 Å) than in **1A** (4.4 Å). There is no C5 group in **2**. Thus, the C5 methylene group will have a greater influence on chemical shifts of the H3 signals in **1B** than in **1A**. In both **1A** and **2**, the C3 methylene group has a similar steric arrangement but different from **1B**.

Chart S1



2 **1A** **1B**

Distance (Å)	**1A**	**1B**
H3A – H5A	4.6	3.8
H3A – H5B	5.3	4.3
H3B – H5B	4.7	3.4
H3B – H5A	**4.4**	**2.4**