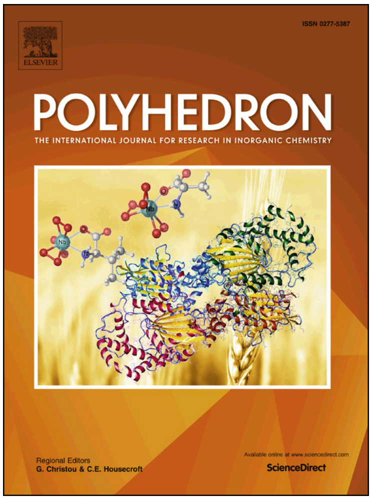

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The synthesis and structural comparison of *fac*-$[Re(CO)_3]^+$ containing complexes with altered β-diketone and phosphine ligands

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Abstract

Six rhenium(I) complexes are structurally compared, with regards to steric and electronic influences induced by the different β-diketone (benzoylacetone – Benzac, trifluoroacetylacetone – Tfaa and hexafluoroacetylacetone – Hfaa) and phosphine ligands (cyclohexyldiphenyl phosphine - PPh_2Cy and dicyclohexylphenyl phosphine - $PPhCy_2$). The complexes *fac*-$[Re(Benzac)(CO)_3(PPh_2Cy)]$ (**2**), *fac*-$[Re(Benzac)(CO)_3(PPhCy_2)]$ (**3**), *fac*-$[Re(Tfaa)(CO)_3(PPh_2Cy)]$ (**5**), *fac*-$[Re(Tfaa)(CO)_3(PPhCy_2)]$ (**6**), *fac*-$[Re(Hfaa)(CO)_3(PPh_2Cy)]$ (**8**) and *fac*-$[Re(Hfaa)(CO)_3(PPhCy_2)]$ (**9**) were synthesized by using the '2+1' mixed ligand approach and characterized by means of IR, UV/Vis, ^1H-, ^{13}C- and ^{31}P NMR and also X-ray diffraction, clearly showing the increase in the carbonyl stretching frequencies and downfield shifts in the ^{31}P NMR as the fluoro atoms on the ligand backbone increases. The Tolman angles for the coordinated phosphine ligands are: **2** = 134.77 °; **3** molecule A = 146.81 °; **5** = 134.46 °; **6** = 146.05 °; **8** = 136.68 ° and **9** = 146.22 °, illustrating the change in steric bulk as the cyclohexyl ligands on the phosphine ligands increase. A direct link is noted between the Re-P distances (2.4906(6) Å for **2**, 2.5213(17) Å for **3** molecule A, 2.4865(16) Å for **5**, 2.5372(15) Å for **6**, 2.4906(14) Å for **8** and 2.5365(16) Å for **9**), *O,O'*-bidentate ligand bite angles, O4-Re-O5, (85.12(6) ° for **2**, 83.34(13) ° for **3** molecule A, 84.91(12) ° for **5**, 83.53(12) ° for **6**, 84.54(11) ° for **8** and 83.7(2) ° for **9**) and the calculated dihedral angles (3.677(1) ° for **2**, 12.521(1) ° for **3** molecule A, 1.489(7) ° for **5**, 12.463(11) ° for **6**, 2.940(7) ° for **8** and 11.747(6) ° for **9**). The dihedral angle is calculated between the equatorial plane (Re1,C1,O1,C2,O2,O4,C5,C6,C7,O5) and the plane through Re1,O4,C5,C6,C7,O5. Dihedral angles of approximately four times larger are observed in complexes with coordinated $PPhCy_2$ ligands compared to the PPh_2Cy containing analogues, indicating the steric effect induced on the bidentate ligand by the extra cyclohexyl substituent on the $PPhCy_2$ ligand.

1. Introduction