Olefin metatheses in metal coordination spheres: versatile new strategies for the construction of novel monohapto or polyhapto cyclic, macrocyclic, polymacrocyclic, and bridging ligands.

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Kolekcja

Naukowa

Streszczenie

The broad applicability of the title reaction is established through studies of neutral and charged, coordinatively saturated and unsaturated, octahedral and square planar rhenium, platinum, rhodium, and tungsten complexes with cyclopentadienyl, phosphine, and thioether ligands which contain terminal olefins. Grubbs' catalyst, [Ru(=CHPh)$(PCy_3)_2(Cl)_2$], is used at 2–9 mol % levels (0.0095–0.00042 M, CH_2Cl_2). Key data are as follows: [(η^5-$C_5H_4(CH_2)_6CH{=}CH_2$)Re(NO)$(PPh_3)(CH_3)$], intermolecular metathesis (95 %); [(η^5-C_5H_5)Re(NO)$(PPh_3)(E(CH_2CH{=}CH_2)_2)]^+$ TfO^- (E=S, PMe, PPh), formation of five-membered heterocycles (96–64 %; crystal structure E=PMe); [(η^5-C_5Me_5)Re(NO)$(PPh((CH_2)_6CH{=}CH_2)_2)(L)]^{n+}$ $n BF_4^-$ (L/*n*=CO/1, Cl/0), intramolecular macrocyclization (94–89 %; crystal structure L=Cl); *fac*-[$(CO)_3$Re(Br)$(PPh_2(CH_2)_6CH{=}CH_2)_2$] and *cis*-[$(Cl)_2Pt(PPh_2(CH_2)_6CH{=}CH_2)_2$], intramolecular macrocyclizations (80–71 %; crystal structures of each and a hydrogenation product); *cis*-[$(Cl)_2$Pt$(S(R)(CH_2)_6CH{=}CH_2)_2$], intra-/intermolecular macrocyclization (R=Et, 55 %/24 %; *t*Bu, 72 %/<4 %); *trans*-[(Cl)(L)M$(PPh_2(CH_2)_6CH{=}CH_2)_2$] (M/L=Rh/CO, Pt/$C_6F_5$) intramolecular macrocyclization (90–83 %; crystal structure of hydrogenation product, M=Pt); *fac*-[$W(CO)_3(PPh((CH_2)_6CH{=}CH_2)_2)_3$], intramolecular trimacrocyclization (83 %) to a complex mixture of triphosphine, diphosphine/monophosphine, and tris(monophosphine) complexes, from which two isomers of the first type are crystallized. The macrocycle conformations, and basis for the high yields, are analyzed.

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