



Cyclopentadienyl/alkoxo ligand exchange in group 4 metallocenes: a convenient route to heterometallic species.

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Streszczenie

A simple and efficient strategy for the synthesis of nonorganometallic heterometallic clusters from cheap organometallic precursors is reported. This unique synthetic method involves elimination of the cyclopentadienyl ring from Cp_2MCl_2 ($\text{M} = \text{Ti, Zr, Hf}$) as CpH in the presence of $\text{M}'\text{I}_2$ or $\text{M}'\text{L}'_2$ ($\text{M}' = \text{Ca, Sr, Mn}$; $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH} = \text{LH}$ or $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH} = \text{L'H}$) in an alcohol as a source of protons. In the reactions presented, a series of compounds, $[\text{Ca}_4\text{Ti}_2(\mu_6\text{-O})(\mu_3, \eta^2\text{-L})_8(\eta\text{-L})_2\text{Cl}_4]$ (**1**), $[\text{Sr}_4\text{Hf}_2(\mu_6\text{-O})(\mu_3, \eta^2\text{-L})_8(\eta\text{-L})_2(\eta\text{-LH})_4\text{Cl}_4]$ (**2**), $[\text{Ca}_4\text{Zr}_2(\mu_6\text{-O})(\mu\text{-Cl})_4(\mu, \eta^2\text{-L})_8\text{Cl}_2]$ (**3**), $[\text{Sr}_4\text{Ti}_2(\mu_6\text{-O})(\mu_3, \eta^2\text{-L})_8(\eta\text{-L})_2(\eta\text{-LH})_2\text{Cl}_4]$ (**4**), $[\text{Ca}_4\text{Zr}_2\text{Cp}_2(\mu_4\text{-Cl})(\mu\text{-Cl})_3(\mu_3, \eta^2\text{-L})_4(\mu, \eta^2\text{-L})_4\text{Cl}_2]$ (**5**), $[\text{CaTiCl}_2(\mu, \eta^2\text{-L}')_3(\eta\text{-L'H})_3][\text{L}']$ (**6**), $[\text{Ca}_2\text{Ti}(\mu, \eta^2\text{-L}')_6\text{Cl}_2]$ (**7**), $[\text{Mn}_4\text{Ti}_4(\mu\text{-Cl})_2(\mu_3, \eta^2\text{-L})_2(\mu, \eta^2\text{-L})_{10}\text{Cl}_6]$ (**8**), and $[\text{Mn}_{10}\text{Zr}_{10}(\mu_4\text{-O})_{10}(\mu_3\text{-O})_4(\mu_3, \eta^2\text{-L})_2(\mu, \eta^2\text{-L})_{16}(\mu, \eta\text{-L})_4(\eta\text{-L})_2\text{Cl}_8]$ (**9**), were obtained in good yield. All of the complexes were characterized by elemental analysis, IR and NMR spectroscopy, and single-crystal X-ray structural analysis. Complex **8** belongs to a group of magnetic clusters that consists of Mn_4 subunits held together by two $\mu\text{-Cl}$ bridges. Compounds **6** and **7** underwent thermal decomposition, yielding an alternative source for some heterometallic oxides, which were analyzed by X-ray powder diffraction.

Adres publiczny

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