Zirconium-molybdenum and titanium-iron bonded organometallic complexes

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The metal carbonylate Na[Mo(η⁵-C₅H₅)(CO)₃] reacts with (η⁵-C₅H₅)₂ZrCl₂ in refluxing THF to give the molybdenum-zirconium bonded compound [(η⁵-C₅H₅)₂Zr{Mo(η⁵-C₅H₅)(CO)₃}₂](I). Whereas Na[Fe(η⁵-C₅H₅)(CO)₃] reacts with (η⁵-C₅H₅)₂TiCl₂ at ambient temperature to yield the iron-titanium bonded compound [(η⁵-C₅H₅)₂Ti{Fe(η⁵-C₅H₅)(CO)₃}₂](II). The compounds I and II have been characterized by IR, PMR, mass spectra and elemental analyses.

Heterobimetallic compounds incorporating transition metals are important because of their potential use in catalysis¹⁻³ and synthetic chemistry⁴⁻⁵. Casey et al.⁶⁻⁷ reported the unbridged metal-metal bonded compounds [(η⁵-C₅H₅)₂Zr{Ru(η⁵-C₅H₅)(CO)₃}₂] and [(η⁵-C₅H₅)₂Zr(CH₃)₂Ru(η⁵-C₅H₅)(CO)₃] from the reactions of Na[Ru(η⁵-C₅H₅)(CO)₃] with (η⁵-C₅H₅)₂ZrCl₂ and (η⁵-C₅H₅)₂Zr(CH₃)₂Cl, respectively, whereas Abys et al.⁸ demonstrated the synthesis of [(η⁵-C₅H₅)₂HfFe(CO)₄]₂, a dimer containing Hf-Fe bond, from the reaction of (η⁵-C₅H₅)₂HfCl₃ with Na₂[Fe(CO)₅]. We report herein the synthesis of metal-metal bonded Zr-Mo and Ti-Fe complexes from the reactions of group IV metal halides with metal carbonylate anions.

**Experimental**

All the reactions and operations were performed under nitrogen atmosphere. Tetrahydrofuran was freshly distilled from sodium and benzophenone prior to use. PMR spectra were recorded on a Varian XL-200 spectrometer and IR spectra on a PE-983 spectrophotometer. The elemental analyses were carried out at the Microanalytical Laboratory, Research School of Chemistry, Australian National University, Australia.

The starting materials Na[Mo(η⁵-C₅H₅)(CO)₃]⁹ and Na[Fe(η⁵-C₅H₅)(CO)₃]¹⁰ were prepared according to the known methods. Dicyclopentadienylzirconium dichloride were purchased from Aldrich and used as received.

**Reaction of Na[Mo(η⁵-C₅H₅)(CO)₃] with (η⁵-C₅H₅)₂ZrCl₂.** Synthesis of [(η⁵-C₅H₅)₂Zr{Mo(η⁵-C₅H₅)(CO)₃}₂](I)

A solution of (η⁵-C₅H₅)₂ZrCl₂ (402 mg, 1.38 mmol) in THF (50 ml) was added dropwise with stirring to a suspension of Na[Mo(η⁵-C₅H₅)(CO)₃] (697 mg, 2.60 mmol) in THF (60 ml) and the reaction mixture was refluxed for 4 h with TLC monitoring. The colour of the solution changed from yellow to red. The solvent was removed in vacuo and the residue extracted with diethyl ether (2 × 20 ml). The combined extract was filtered through kieselguhr and the filtrate concentrated in vacuo to give a reddish yellow solid which was chromatographed over silica gel, eluting with pet. ether (40-60°) to yield the product [(η⁵-C₅H₅)₂Zr{Mo(η⁵-C₅H₅)(CO)₃}₂](I) as red crystals (208 mg, 21%).

**Results and discussion**

The reaction of (η⁵-C₅H₅)₂ZrCl₂ with Na[Mo(η⁵-C₅H₅)(CO)₃] in refluxing THF gives [(η⁵-C₅H₅)₂Zr{Mo(η⁵-C₅H₅)(CO)₃}₂](I) while the reaction of (η⁵-C₅H₅)₂TiCl₄ with Na[Fe(η⁵-C₅H₅)(CO)₃] at ambient temperature yields [(η⁵-C₅H₅)₂Ti{Fe(η⁵-C₅H₅)(CO)₃}₂] (II). The structures of the metal-metal bonded compounds (I) and (II) have been elucidated on the basis of IR, PMR, mass spectroscopic data and elemental analyses.

The mass spectrum of I showed the molecular ion peak (based on ⁹⁰Zr and ⁹⁰Mo) at m/z 714 and other important
peaks at m/z 686 (M⁺ - CO), 621[M⁺-(CO+C₅H₅)], 593 [M⁺-(2CO+C₅H₅)], 565[M⁺-(3CO+C₅H₅)], 500 [M⁺-(3CO+2C₅H₅)], 435[M⁺-(3CO+3C₅H₅)], 370[M⁺-(3CO+4C₅H₅)], 342[M⁺-(4CO+4C₅H₅)], 314[M⁺-(5CO+4C₅H₅)] and 286[M⁺-(6CO+4C₅H₅)].

The mass spectrum of II did not exhibit the molecular ion peak at m/z 532 (based on ⁴⁸Ti and ⁵⁶Fe); instead it showed peaks at m/z 504 arising by the rapid loss of one CO group from the parent and other important peaks at m/z 439[M⁺-(CO+C₅H₅)], 411[M⁺-(2CO+C₅H₅)], 383[M⁺-(3CO+C₅H₅)], 342[M⁺-(4CO+C₅H₅)], 188[M⁺-(5CO+4C₅H₅)] and 104[M⁺-(6CO+4C₅H₅)].

These fragmentation patterns are characteristics of metal carbonyl complexes.

The shift of the ν(CO) bands of I (in cyclohexane, 1999 emissions at 1974 and 1958 cm⁻¹) and II (in cyclohexane, 2002s and 1957s cm⁻¹) to higher energies from the corresponding bands of Na[M(η⁵-C₅H₅)₂Zr(CH₃)₂Ru(η⁵-C₅H₅)(CO)]₂ which has been shown by X-ray crystallography to contain a Zr-Ru bond. The PMR spectra of I [CD₂Cl₂, δ 5.36 (s, 10H) and 5.44 (s, 10H) ppm] and II [CD₂Cl₂, δ 5.00 (s, 10H) and 3.99 (s, 10H) ppm] indicated the presence of two types of cyclopentadienyl protons; in each case the former has been assigned to [(η⁵-C₅H₅)₂M (M = Zr or Ti)] protons and the latter for protons of (η⁵-C₅H₅)₂M (M = Mo or Fe) units. These assignments are based on the chemical shifts of the cyclopentadienyl protons of some closely related compounds.

It is clear from the present study that the reactivity of the metal carbonylate anions toward Lewis acid depends on the nucleophilicity of the anion. Thus the anion Na[Fe(η⁵-C₅H₅)(CO)₂] being highly nucleophilic reacts readily as compared to the weak nucleophile Na[Mo(η⁵-C₅H₅)(CO)₃].

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References