Anal. Calcd. for $C_{15}H_{20}Fe$: C, 70.33; H, 7.87. Found: C, 70.51; H, 7.79. [^{1}H-NMR C_6D_6, 100 MHz ppm: 1.87 (15H, s), 3.52 (5H, s).]

Properties

This mixed metallocene is air-stable as a dry solid and melts at 89–90°C. It oxidizes slowly in solutions exposed to the air. It is very soluble in pentane, benzene, THF, and diethyl ether. It can be recrystallized from methanol. It sublimes without appreciable decomposition.

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33. PYRAZOLATE-BRIDGED RUTHENIUM(I) CARBONYL COMPLEXES

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The number of known ruthenium(I) carbonyl complexes is relatively small in comparison to those known for ruthenium(0) or ruthenium(II).[1] Moreover, apart from $[Ru_2(C_5H_5)_2(CO)_4]$[2] and carboxylato complexes of the type $[Ru_2(\mu\text{-}RCO_2)_2(CO)_4L_2]$,[3] whose syntheses are well established, most of the

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other ruthenium(I) carbonyl compounds have been obtained in low yields, generally as by-products of reactions of $[Ru_3(CO)_{12}]$ or other polynuclear clusters.[1,4] We describe here a simple synthesis of the complexes $[Ru_2(\mu\text{-L})_2(CO)_6]$ [L = 3,5-dimethylpyrazolato (Me_2pz) and pyrazolato (pz)], starting from $RuCl_3 \cdot nH_2O$,[5] the cheapest starting material for ruthenium compounds, in higher yields than those reported starting from the more expensive $[Ru_3(CO)_{12}]$.[6] Several ruthenium(I) carbonyl complexes are efficient catalyst precursors for the homogeneous hydroformylation of olefins[7] and for the addition of carboxylic acids to alkynes.[8]

■ **Caution.** *All the manipulations must be carried out with the use of gloves in an efficient fume hood due to the toxicity of* $RuCl_3 \cdot nH_2O$ *and carbon monoxide. The 2-methoxyethanol used should be free of peroxides.*[9]

A. BIS(μ-3,5-DIMETHYLPYRAZOLATO-N^1: N^2)-BIS[TRICARBONYLRUTHENIUM(I)] (*Ru-Ru*)

$$RuCl_3 \cdot nH_2O + CO + CH_3OCH_2CH_2OH \rightarrow \text{“yellow solution”}$$

$$\text{“yellow solution”} + Me_2pzH + Zn + CO \rightarrow [Ru_2(\mu\text{-}Me_2pz)_2(CO)_6] + H_2 + ZnCl_2$$

Procedure

A 100-mL reaction flask equipped with a gas inlet and a reflux condenser connected to a mineral oil bubbler is charged with $RuCl_3 \cdot nH_2O$* (3 g, 10.74 mmol) and 2-methoxyethanol (60 mL). Carbon monoxide is bubbled through the initially brown solution at reflux temperature until the color is pale yellow† (2–3 h). Then, 3,5-dimethylpyrazole‡ (1.102 g, 10.74 mmol) and granular zinc‡ (5 g) are added (the use of zinc dust reduces the yield of the final product). The mixture is stirred at reflux temperature maintaining a slow stream of carbon monoxide. After 2 h, the mixture is cooled to room temperature and the pale brown-grey suspension is decanted from the unreacted zinc and poured under air into a beaker containing 200 mL of distilled water. The yellowish precipitate is collected by filtration with a sintered-glass filter, washed with water (five 10-mL portions), and dried by suction. This solid is dissolved in the filter in the minimum volume of dichloromethane and the solution is chromatographed on a silica gel (Merck, 35–70 mesh) column

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* Obtained from Johnson Matthey, 38.7% Ru.

† The composition of this yellow solution is uncertain; however, it has proven to be a useful source of mononuclear ruthenium(II) carbonyl complexes (ref. 1, p. 693).

‡ Obtained from Aldrich.

(15 × 3 cm). Elution with hexane affords two bands. The first one is yellow and contains a small amount of a mixture of $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$. The second one is colorless and moves very slowly with hexane and the eluant is changed to hexane–dichloromethane (1 : 1).* Vacuum removal of the solvent gives the product as white crystals. Yield 2.65 g (82%).

Anal. Calcd. for $C_{16}H_{14}N_4O_6Ru_2$: C, 34.3; H, 2.5; N, 10.0. Found: C, 34.5; H, 2.6; N, 9.8.

B. BIS(μ-PYRAZOLATO-N^1: N^2) BIS[TRICARBONYLRUTHENIUM(I)] (*Ru-Ru*)

Procedure

This compound is prepared by the same procedure as that described for $[Ru_2(\mu\text{-}Me_2pz)_2(CO)_6]$, in 65% yield.

Anal. Calcd. for $C_{12}H_6N_4O_6Ru_2$: C, 28.9; H, 1.2; N, 11.1. Found: C, 28.9; H, 1.1; N, 11.1.

Properties

Both compounds are white air-stable solids, which are very soluble in acetone, ethers, chlorinated solvents, and aromatic hydrocarbons, slightly soluble in alcohols and aliphatic hydrocarbons, and insoluble in water. On heating, they decompose without melting. Spectroscopic data for $[Ru_2(\mu\text{-}Me_2pz)_2(CO)_6]$: ν(CO) (hexane): 2089(m), 2057(s), 2013(vs), 1998(m), 1971(w), 1964(w) cm^{-1}. ^1H NMR ($CDCl_3$): 5.60 (s, 2H), 2.10 (s, 12H) ppm. Fast atom bombardment (FAB) mass spectrum (m/z): 560 (M^+) and the successive loss of six CO groups. Spectroscopic data for $[Ru_2(\mu\text{-}pz)_2(CO)_6]$: ν(CO) (hexane): 2094(m), 2062(s), 2018(vs), 2005(m), 1982(w), 1969(w) cm^{-1}. ^1H NMR ($CDCl_3$): 7.29 (d, $J = 2.1$ Hz, 4H), 6.07 (t, $J = 2.1$ Hz, 2H) ppm. FAB mass spectrum (m/z): 504 (M^+) and the successive loss of six CO groups. The X-ray structure of the Me_2pz complex has been reported.[5] Both compounds present a rich and somewhat different derivative chemistry; that is, both can be oxidized with iodine to give $[Ru_2(\mu\text{-}I)(\mu\text{-}L)_2(CO)_6]I_3$,[5] but upon reaction with phosphine ligands the pz complex gives the disubstituted derivatives $[Ru_2(\mu\text{-}pz)_2(CO)_4(PR_3)_2]$[6] while the Me_2pz complex only affords the monosubstituted ones $[Ru_2(\mu\text{-}Me_2pz)_2(CO)_5(PR_3)]$.[5] The complex

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* The elution of the colorless band can be monitored by qualitative TLC, observing the plates under UV light, or by running periodical IR spectra of the eluted solution.

$[Ru_2(\mu\text{-}pz)_2(CO)_4(PPh_3)_2]$ can also be prepared by reaction of $[Ru_3(CO)_9(PPh_3)_3]$ with pyrazole in refluxing toluene.[10]

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34. MAIN GROUP-TRANSITION METAL CARBONYL COMPLEXES

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Metal carbonyl anions react with main group halides and oxides to yield a number of main-group transition-metal carbonyl complexes in good yields. These complexes serve as starting materials for a number of higher nuclearity cluster complexes.

General Procedure

All operations are carried out under an inert atmosphere using standard Schlenk line techniques.[1] Either deionized or distilled water which has been

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