ELECTRONIC SUPPORTING INFORMATION

Easy Activation of Two C–H Bonds of an N-Heterocyclic Carbene

N-Methyl Group

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Synthetic and Analytical Details of Compounds 1 and 2

General: Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons), or calcium hydride (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC (silica gel). [Me₂ImH]I was prepared by treating 1-methylimidazole with methyl iodide⁴ and was handled in a dry box. IR: Perkin-Elmer FT 1720-X. NMR: Bruker DPX-300, room temperature, TMS as internal standard. Microanalyses: Perkin-Elmer 2400. MS: VG Autospec double-focussing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs⁺ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix; data given refer to the most abundant molecular ion isotopomer.

[Ru₃(Me₂Im)(CO)₁₁] (1): A mixture of [Me₂ImH]I (350 mg, 1.5 mmol) and KO'Bu (176 mg, 1.5 mmol) was stirred in THF (60 mL) for 30 min. Powdered [Ru₃(CO)₁₂] (1 g, 1.5 mmol) was then added and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane (2 x 2 mL). This solution was separated by column chromatography (20 x 3 cm) on silica gel. Hexane eluted some unreacted [Ru₃(CO)₁₂]. Hexane-dichloromethane (4:1) eluted the major band (orange-red), which gave compound 1 after solvent removal (578 mg, 55%).

Data for 1: IR (CH₂Cl₂, cm⁻¹): ν(CO) = 2093 (m), 2038 (vs), 2019 (vs), 2005 (s), 1975 (m, sh), 1949 (w, sh); ¹H NMR (300 MHz, 293 K, CDCl₃): δ = 7.02 (s, 1 H), 3.80 (s, 3 H). ¹³C{¹H} NMR (75 MHz, 293 K, CDCl₃): δ = 204.9 (NCN), 123.6 (CH), 40.2 (Me). FAB-MS: m/z = 709 [M⁺]; elemental analysis calcd (%): C₁₆H₈N₂O₁₁Ru₃ (707.45): C 27.16, H 1.14, N 3.96; found C 27.22, H 1.18, N 3.87.

[Ru₃(µ-H)₂(µ₃-MeImCH)(CO)₉] (2): A solution of compound 1 (500 mg, 0.7 mmol) in THF (60 mL) was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (2 x 2 mL). This solution was separated by column chromatography (25 x 3 cm) on silica gel. Hexane-dichloromethane (4:1) eluted a small amount of compound 1 followed by a major bright orange band, which gave compound 2 after solvent removal (290 mg, 63%). Further elution of the column with
hexane-dichloromethane (2:1) afforded two minor brown bands containing two as yet unidentified products.

*Data for 2:* IR (CH$_2$Cl$_2$, cm$^{-1}$): ν(CO) = 2093 (m), 2063 (s), 2038 (vs), 2010 (m), 1998 (m), 1984 (m), 1965 (w, sh); $^1$H NMR (300 MHz, 293 K, CDCl$_3$): δ = 6.88 (s, 1 H), 6.86 (d, $J = 1.8$, 1 H), 6.41 (d, $J = 1.8$, 1 H), 3.55 (s, 3 H), –12.64 (d, $J = 2.6$, 1 H), –16.63 (d, $J = 2.6$, 1 H); $^{13}$C($^1$H) NMR (75 MHz, 293 K, CD$_2$Cl$_2$): δ = 170.3 (NCN), 119.9 (CH), 119.6 (CH), 104.7(CH), 37.9 (Me). FAB-MS: $m/z = 653 \ [M^+]$; elemental analysis calcd (%) for C$_{14}$H$_8$N$_2$O$_9$Ru$_3$ (651.53): C 25.81, H 1.24, N 4.30; found C 25.86, H 1.27, N 4.28.

**Reaction of Compound 2 with Carbon Monoxide:** Carbon monoxide was gently bubbled through a solution of compound 2 (30 mg) in THF (15 mL). After 40 min, an IR spectrum showed that compound 1 was the only complex in the solution.

**X-Ray Crystallographic Studies on Compounds 1 and 2:** Intensity measurements were made with a Bruker AXS SMART 1000 diffractometer using graphite monochromatized Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to 2θ = 48.6°. Raw frame data were integrated with the SAINT+ program.$^2$ The structures were solved by direct methods with SHELXTL.$^3$ A semi-empirical absorption correction was applied with the program SADABS.$^4$ All non-hydrogen atoms were refined anisotropically. The hydride ligands H(100) and H(200) of compound 2 were located from difference maps and were freely refined (x, y, z, and U$_{iso}$). The remaining H atoms of 1 and 2 were geometrically positioned and refined using a riding model.
References


(2) *SAINT+*, *SAX Area Detector Integration Program*, version 6.02, Bruker AXS Inc., Madison, WI, **1999**.


(4) G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Göttingen, Göttingen, Germany, **1997**.