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LETTER

The First Heteronuclear Monoazadiene Complex: Synthesis and X-ray Crystal Structure of $HFeRu(CO)_5(R{-}C{=}CH{-}CH{=}N{-}iPr)$, Isolobally Related to $HFe(CO)_2(\eta^5\text{-}C_5H_5)$

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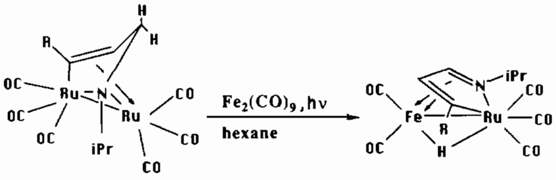
There has been considerable interest in the preparation of polymetallic complexes because of their model function in heterogeneous catalysis as well as their potential role in homogeneous catalysis [1]. Heterometallic compounds are particularly important in this respect because they might show unique reactivity as a result of the synergistic combination of different properties of the constituent metals.

Our interest is focussed on the preparation of homo- and heterometallic complexes containing the conjugated monoazadiene ligand (MAD, representing the C=CC=N skeleton) and its derivatives. The organometallic chemistry of MAD has thus far been limited to mononuclear [2] and homopolynuclear complexes [3,4]. In particular, the latter show the interesting feature of MAD to undergo various C–H activation and H-migration reactions. As the coordination of MAD to two (or more) different metals in heteronuclear complexes may provide new possibilities for such fundamental reactions, we attempted the synthesis of heteronuclear compounds containing the MAD ligand.

As an entry to this type of heteronuclear chemistry, compound **1** (Scheme 1), which is formed in the first stage of the reaction of $Ru_3(CO)_{12}$ with MAD [5], is used. The known photochemical reactivity of **1** with CO, resulting in CO-insertion in the Ru–N bond [5], led us to explore the photochemically induced reaction of **1** with the $Fe(CO)_4$ unit, which is isolobal to an organic or bridging CO fragment.



1 **1a**, **2a**: R = Ph **2**
1b, **2b**: R = Me

Scheme 1.

Experimental

A hexane solution of 1 mmol of $Ru_2(CO)_6(CH_3{-}C{=}CH{-}CH_2{-}N{-}R)$ (**1**) (**1a**, R = Ph; **1b**, R = Me) was irradiated in the presence of about an eightfold molar excess of suspended $Fe_2(CO)_9$ at room temperature over 2 h (75% conversion of **1**). As light source a high pressure mercury lamp was used in combination with a filter (2-cm path length of a 0.25 M water solution of $CoSO_4 + NiSO_4$ in pyrex glass, being transparent in the wavelength region 290–350 nm), in order to prevent **2** from further photoreactions as much as possible. The UV absorption of **1** at 334 nm, which probably corresponds to the photoreactive transition, falls within the window of the filter. This reaction resulted in the formation of a mixture of products, which could be partly separated by column chromatography on silica. With hexane/dichloromethane (20:1) as eluent, an orange fraction was obtained containing a mixture of $HFeRu(CO)_5(R{-}C{=}CH{-}CH{=}N{-}iPr)$ (**2**) and $H_2FeRu_3(CO)_{13}$. The air-sensitive compound **2** could be purified by selectively crystallizing $H_2FeRu_3(CO)_{13}$ from a dilute hexane solution at 193 K. Crystals of **2** were obtained in about 35% yield by crystallization from a concentrated hexane solution at 193 K. Other column fractions contained some starting complex **1**, $Fe_2Ru(CO)_{12}$ and small amounts of another heteronuclear MAD complex, which was analyzed as $FeRu_3(CO)_{10}(R{-}C{=}CH{-}CH{=}N{-}iPr)_2$ (by FD–mass spectrometry). Correct elemental analyses and FD–mass data for compound **2** have been obtained. Important NMR data (δ ($Me_4Si = 0$) in ppm, numbering corresponds to the C atom numbering in Fig. 1): **2a**, ^1H NMR (C_6D_6, 250.1 MHz) 5.71 ($1H_{9,10}$, d, $J_{9,10} = 1.5$ Hz), 5.66 ($1H_{9,10}$, d, $J_{9,10} = 1.5$ Hz), 2.02 ($1H_6$, sept., $J_{6-7,8} = 6.5$ Hz), −9.12 ($1H_1$, s);

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^{13}C NMR (C_6D_6, 62.9 MHz) 215.0, 212.9 ($C_{4,5}$), 195.0, 191.6, 190.7 ($C_{1,2,3}$); 109.1, 103.6 ($C_{9,10}$); **2b**, ^1H NMR ($CDCl_3$, 100.1 MHz) 6.48 ($1H_9$, d, $J_{9,10} = 1.7$ Hz), 5.84 ($1H_{10}$, br), 2.53 ($1H_6$, sept, $J_{6-7,8} = 6.5$ Hz), −9.40 ($1H_1$, s); ^{13}C NMR (62.9 MHz, toluene-d_8, 263 K) 215.7, 214.9 ($C_{4,5}$); 196.7, 192.4, 190.8 ($C_{1,2,3}$); 149.7 (C_{11}); 109.4, 105.8 ($C_{9,10}$).

The molecular structure of **2b** has been determined by single-crystal X-ray diffraction. Crystal data: crystals of $C_{12}FeH_{13}NO_5Ru$ are monoclinic, space group $P2_1/c$, $Z = 4$; $a = 13.242(2)$, $b = 9.801(2)$, $c = 12.212(3)$ Å; $V = 1548(2)$ Å^3, $\beta = 102.3(2)$, $\mu(\text{Cu K}\alpha) = 158.0$ cm^{-1}, $d_{calc} = 1.75$ g cm^{-3}. Crystal dimensions 0.12 × 0.25 × 0.25 mm. A total of 1568 intensities were measured on a Nonius CAD-4 diffractometer using graphite monochromated Cu Kα radiation ($\lambda = 1.5418$ Å; $2.5 \leqslant \theta \leqslant 50\infty$; h, −13 to 13; k, 0 to 9; l, 0 to 12). Of these, 590 were below the 2.5 $\sigma(I)$ level and were treated as unobserved. The Fe and Ru atoms were found by means of the symbolic-addition program set SIMPEL [6]. The remaining non-hydrogen atoms were found by subsequent Fourier syntheses. Refinement proceeded by means of anisotropic block-diagonal least-squares calculations. The H atoms were introduced at their calculated positions and not refined. An empirical absorption correction was applied (DIFABS) [7]. The final R value was 0.053 ($R_w = 0.076$). A weighting scheme $w = (40 + F_o + 0.01F_o^2)^{-1}$ was applied. The calculations were carried out with XRAY76 [8]. The scattering factors and the dispersion correction factors were taken from the literature [9, 10].

Results and Discussion

Upon photochemical reaction of **1** with $Fe_2(CO)_9$ (as a source of $Fe(CO)_4$), the resulting compound appeared not to be an $FeRu_2$ cluster due to insertion of $Fe(CO)_4$ into the Ru–N or Ru–C bond, analogous to the CO-insertion reaction of **1**, but the heterodinuclear MAD complex **2** with stoichiometry HFeRu(CO)$_5$(R–C=CH–CH=N–iPr) (**2a**, R = Ph; **2b**, R = Me). The unexpected novel compound **2** is very interesting because of its heteronuclear character, which is unprecedented in the chemistry of MAD.

The major geometric features of **2** can be inferred from the spectroscopic data, especially the ^{13}C NMR spectra and have been confirmed by a single-crystal X-ray diffraction study (Fig. 1).

The π-coordination of MAD is clearly reflected in the characteristic large upfield shift (30–50 ppm) of C_9 and C_{10}, compared to the free ligand. The presence of an $Fe(CO)_2$ unit and a $Ru(CO)_3$ moiety was indicated by two ^{13}C resonances at about 215 ppm and three around 192 ppm, respectively. These data point to σ-coordination of MAD to Ru and π-coordination to Fe. The ^1H NMR spectra of **2** show a signal at about −9 ppm, revealing the presence of a hydride. So, in the overall reaction of **1** with $Fe_2(CO)_9$ net activation of one of the methylene C–H bonds in **1** has occurred, resulting in the formation of a metal hydride. From similar complexes in the literature, e.g. the $Ru_2(CO)_6$ complex of benzylideneacetone, it is known that hydrides in this kind of complexes have the possibility of bridging the metal–metal bond [11]. The chemical shift position of the hydride at −9 ppm neither

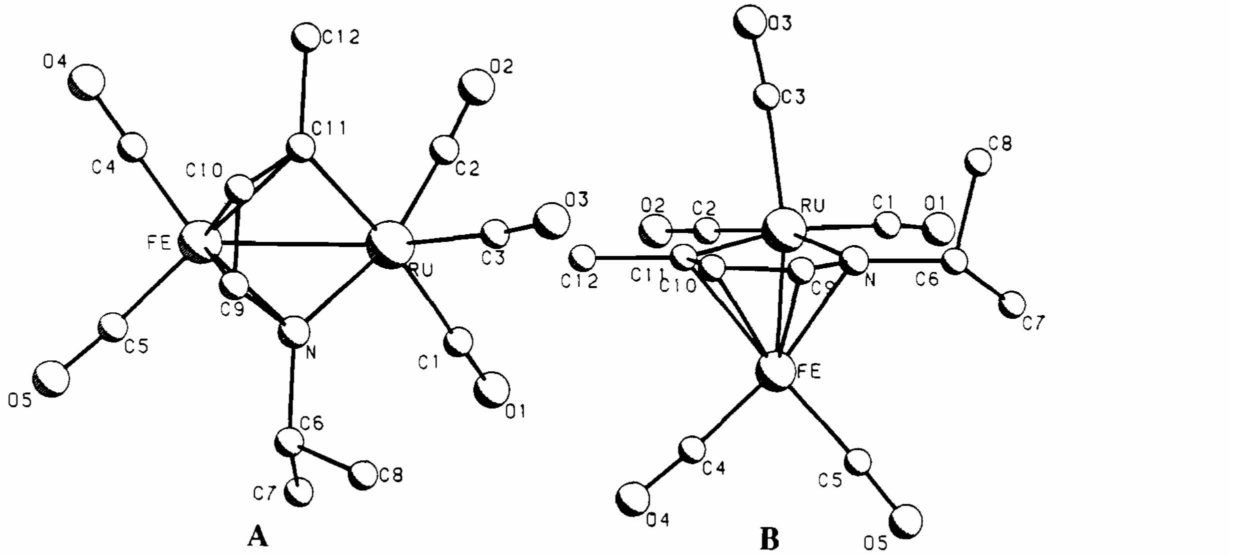

Fig. 1. Pluto drawings of **2b**. Selected bond distances (Å): Fe–Ru, 2.590(3); Ru–N, 2.11(1); Ru–C_{11}, 2.08(2); Fe–N, 2.04(1); Fe–C_9, 2.04(2); Fe–C_{10}, 2.07(2); Fe–C_{11}, 2.12(2); N–C_9, 1.36(2); C_9–C_{10}, 1.35(3); C_{10}–C_{11}, 1.36(3).

indicates nor excludes its bridging character. Unfortunately, the quality of the X-ray diffraction data was not sufficient to allow the location of any hydrogen atoms, including the hydride. However, the observed non-reactivity of the Fe–H bond in a reaction of 2 with CCl_4, which is known for its rapid H/Cl exchange reactions with terminal hydrides (see e.g. ref. 12), points to the bridging character of this hydrogen atom.

The MAD ligand bridges the Fe–Ru bond in a formally seven-electron donating coordination mode, σ-C, σ-N coordinated to Ru and attached to Fe by the conjugated olefin–imine π-system. A representation of the molecular framework of **2b** is provided in view A in Fig. 1. The Fe–Ru distance of 2.590(3) Å indicates a single Fe–Ru bond [13]. View B in Fig. 1 clearly illustrates the planarity of the five-membered $Ru–N–C_{11}–C_{10}–C_9$ ring. The largest deviation from this plane amounts to 0.06 Å (for C_{11}, standard deviation of the fit 0.054). As has been described previously [4b], such a five-membered metallacycle is isolobal to the cyclopentadienyl ring, so the heteronuclear compound 2 is isolobally related to $HFe(CO)_2Cp$. Apart from this theoretical similarity between $HFe(CO)_2Cp$ and 2, the ruthena-azacyclopentadienyl ring in 2 is, like the cyclopentadienyl ring, able to change its hapticity from η^5 to η^3. This hapticity change could be brought about by placing 2 under 40 bar of CO pressure. The reaction was followed by ^1H NMR in a pressurizable sapphire 10-mm tube at 303 K. One of the resulting species in solution was identified as $HFeRu(CO)_6(R–C=CH–CH=N–iPr)$ (as indicated by the downfield shifted resonance of H_9 at about 7.0 ppm and the hydride resonance at about -16 ppm), in which now a third CO ligand is coordinated to Fe instead of the formerly η^2-coordinated C=N moiety. Hence the η^5-$Ru–N–C_{11}–C_{10}–C_9$ heterocycle in 2 has become η^3-$Ru–C_{11}–C_{10}$ coordinated to Fe. Further research in this field of heteronuclear organometallic chemistry is in progress.

Acknowledgements

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