Journal of Organometallic Chemistry, 426 (1992) C36–C39
Elsevier Sequoia S.A., Lausanne
JOM 22548

Preliminary communication

A diruthenium complex containing an *ortho*-metallated bipyridyl ligand formed directly from $[Ru_3(CO)_{12}]$ and pyridine

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(Received December 3, 1991)

Abstract

The cluster $[Ru_3(CO)_{12}]$ reacts with pyridine (6 mol/mol Ru_3) at 120°C to give $[Ru_2(\mu\text{-pyr})_2(CO)_6]$ (pyr = 2-pyridyl, C_5H_4N) as head-to-head and head-to-tail isomers and with neat pyridine at 180°C to give $[Ru_2(\mu\text{-pyr})(\mu\text{-}C_{10}H_7N_2)(CO)_5]$, shown by X-ray diffraction to contain a bridging orthometallated bipy ligand formed by coupling of two 2-pyridyl ligands.

Pyridine is orthometallated by reaction with $[Os_3(CO)_{12}]$ under fairly mild conditions to give the trinuclear clusters: $[Os_3(\mu\text{-H})(\mu\text{-pyr})(CO)_{10}]$, $[Os_3(\mu\text{-H})(\mu\text{-pyr})(CO)_9(py)]$, and $[Os_3(\mu\text{-H})_2(\mu\text{-pyr})_2(CO)_8]$ (pyr = 2-pyridyl) [1] and related 2-pyridyl clusters are formed from $[Ru_3(CO)_{12}]$ [2,3]. More forcing conditions, such as heating a neat pyridine solution of $[Os_3(CO)_{12}]$ at 180°C in a sealed glass tube, gave a quantitative yield of isomers of $[Os_2(\mu\text{-pyr})_2(CO)_6]$ in approximately equal amounts, identified by XRD studies of the 4-methylpyridine analogues as head-to-head and head-to-tail isomers [4]. $[Ru_3(CO)_{12}]$ is generally much more reactive than $[Os_3(CO)_{12}]$ and reacts with pyridine (6 mol/mol Ru_3) in n-heptane at 120°C for 72 h to give a complex product mixture from which the only species we have so far isolated is $[Ru_2(\mu\text{-pyr})_2(CO)_6]$, **1** (27%). Careful TLC on silica eluting with light petroleum (b.p. 30–40°C) allowed total separation of the 1:1 mixture of head-to-head **1a** and head-to-tail **1b** isomers as colourless crystals. $^{13}C\{^1H\}$ NMR spectra [5*] gave four carbonyl resonances with intensity ratio 2:2:1:1 (w, x, y, z) for **1a** and three absorptions with intensity ratio 2:2:2 (x, y, z) for **1b** (Scheme 1).

Attempting to improve the yields of **1a** and **1b**, we carried out a reaction under the same conditions that we had used earlier for osmium (neat pyridine, 180°C,

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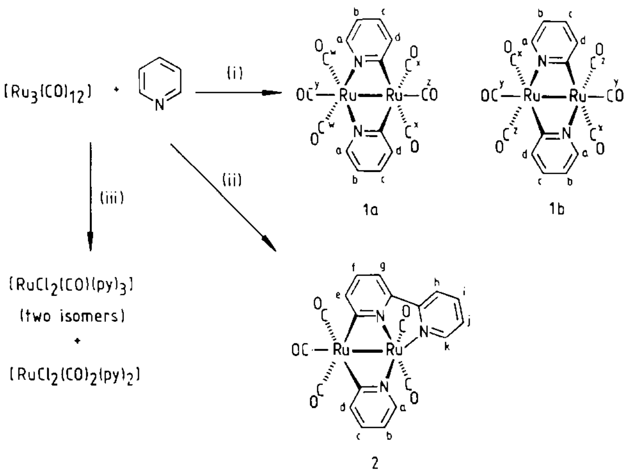
* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

6 h) and obtained much intractible material as well as red crystals of compound **2** (12%) [6*]. A similar reaction with 4-methylpyridine gave **3** (16%) analogous to **2**. These compounds were characterised as $[Ru_2(\mu\text{-}RC_5H_3N)(\mu\text{-}R_2C_{10}H_5N_2)(CO)_5]$, **2** (R = H) or **3** (R = Me) by ^1H NMR, IR, [5*] and XRD in the case of compound **2** [7*]. The ^1H NMR spectrum of **2** contains 11 equal intensity multiplets and thus four H-atoms have been lost from three pyridine rings in the formation of **2**. An analysis of the spectrum was consistent with two 2-pyridyl rings and a third ring with just three adjacent H-substituents. The crystal structure of **2** was determined by X-ray diffraction (Fig. 1); the compound contains two organic ligands: pyridine and 2,2′-bipyridyl ligands both orthometallated at sites adjacent to nitrogen atoms. Unlike compound **1**, it is clear from NMR data that compound **2** exists as a single isomer. The X-ray structure refines best with all three N-atoms attached to Ru(2), that is just one of the two possible orientations of the 2-pyridyl bridge. 2-Pyridyl ligands do not easily re-orientate [8], for example, enantiomers of $[Os_3(\mu\text{-}H)(\mu\text{-}pyr)(CO)_{10}]$ have been resolved and do not interconvert [9]. Although **2** may be the kinetically-controlled isomer with the 2-pyr ligand locked in that particular orientation, it is more likely that the most stable product is obtained at the elevated temperatures used in the preparation.

The *ortho*-metallated bipy ligand is the same as that found in the cluster $[Os_3(\mu\text{-}H)(\mu\text{-}C_{10}H_7N_2)(CO)_9]$, **4** [10], although in that case the cluster was formed directly from bipy and not through the coupling of 2-pyridyl units as in the formation of **2** and **3**. The ruthenium analogue of **4** is also known [11] and its structure is probably like that of **4** although this has not been established by diffraction methods.

Use of even more forcing conditions for the reaction between $[Ru_3(CO)_{12}]$ and pyridine to induce further C–C bond coupling (neat pyridine, 180°C, 49 h) led to a very reactive mixture. Opening of the evacuated reaction tube, removal of pyridine under reduced pressure, and extraction of the residue into dichloromethane before TLC separation gave the known complexes $[RuCl_2(CO)_2(py)_2]$ (8%) [12] and

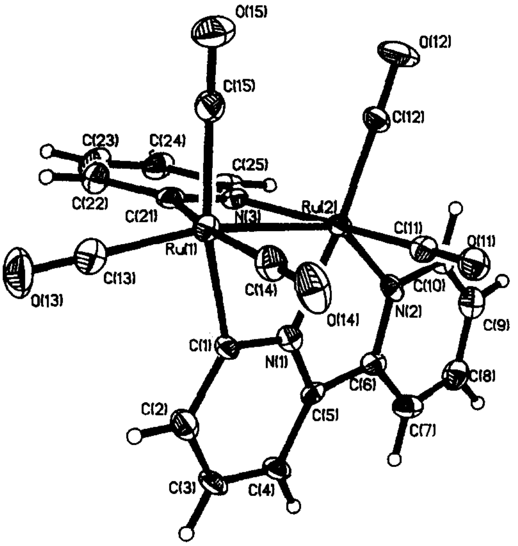


Fig. 1. Molecular structure of the complex $[Ru_2(\mu\text{-}C_5H_4N)(\mu\text{-}C_{10}H_7N_2)(CO)_5]$, compound 2. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(2) 2.715(2), Ru(1)-C(21) 2.12(1), Ru(1)-C(1), 2.11(1), Ru(2)-N(1) 2.04(1), Ru(2)-N(2) 2.23(1), Ru(2)-N(3) 2.13(1), C(21)-Ru(1)-Ru(2) 70.6(4), C(1)-Ru(1)-Ru(2) 70.5(4), N(1)-Ru(2)-Ru(1) 70.3(3), N(3)-Ru(2)-Ru(1) 71.1(3), N(2)-Ru(2)-Ru(1) 143.3(3), N(1)-Ru(2)-N(2) 74.6(4), C(1)-Ru(1)-C(21) 84.2(5), N(1)-Ru(2)-N(3) 82.5(4), N(2)-Ru(2)-N(3) 94.3(4).

$[RuCl_2(CO)(py)_3]$ which has been reported in one isomeric form [13] although we obtained two isomers (58 and 11%) that were separable by TLC. We are examining the nature of the material that reacts so readily with dichloromethane to give these ruthenium(II) complexes.

Acknowledgement. We thank the S.E.R.C. for a grant towards the diffractometer and for a research studentship (for B.R.C.).

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5 Selected spectroscopic data (IR in cyclohexane, NMR in $CDCl_3$, 400 MHz, 292 K, measured J in Hz). Compound **1a**: ν(CO)/cm^{-1}: 2071s, 2033vs, 2004vs, 1985m, 1967s; ^{1}H NMR: δ 7.94 (ddd, H^a, J = 5.5, 1.6, 0.9), 7.32 (ddd, H^d, J = 7.4, 1.2, 1.2), 7.13 (ddd, H^c, J = 7.6, 7.6, 1.7), 6.71 (ddd, H^b, J = 7.3, 5.6, 1.5); ^{13}C NMR: δ 204.6, 201.7, 183.3, 196.1 or 185.9 (CO ligands), 196.1 or 185.9, 154.5, 139.1, 132.9, 119.4 (μ-pyr ligands). Compound **1b**: ν(CO)/cm^{-1}: 2071s, 2034vs, 2003vs, 1985m, 1974s, 1968s; ^{1}H NMR: δ 7.87 (ddd, H^a, J = 5.5, 1.6, 0.9 Hz), 7.38 (ddd, H^d, J = 7.4, 1.2, 1.2 Hz), 7.17 (ddd, H^c, J = 7.5, 7.5, 1.7 Hz), 6.73 (ddd, H^b, J = 7.3, 5.6, 1.5 Hz); ^{13}C NMR: δ 204.3, 202.0, 183.7 (CO ligands), 190.2, 154.8, 138.7, 133.0, 120.1 (μ-pyr ligands). Compound **2**: ν(CO)/cm^{-1}: 2051m, 1996s, 1981vs, 1958m, 1926m; ^{1}H NMR: δ 9.28 (ddd, H^a, J = 5.4, 1.6, 0.9), 7.98 (dd, H^d, J = 8.1, 1.9), 7.94 (ddd, H^c, J = 8.0, 8.0, 1.6), 7.61 (ddd, H^k, J = 5.4, 1.7, 1.0), 7.56 (dd, H^e, J = 6.6, 2.0), 7.52 (ddd, H^b, J = 6.1, 5.2, 1.8), 7.34 (dd, H^g, J = 7.6, 1.9), 7.31 (dd, H^f, J = 7.5, 7.5), 7.24 (dd,

H^h, $J = 7.5$, 1.2), 6.96 (ddd, H^i, $J = 7.5$, 7.5, 1.7), 6.49 (ddd, H^j, $J = 7.3$, 5.6, 1.4).

6 Synthesis of compounds **2**. Triruthenium dodecacarbonyl (0.225 g) and pyridine (20 cm^3) were sealed in an evacuated glass tube which was heated at 180°C for 6 h. The red solution was reduced to dryness under reduced pressure and the residue was separated by TLC on silica [eluant: light petroleum (b.p. 30–40°C)/dichloromethane (1:1 v/v)] to give one main red band which gave red crystals of $[Ru_2(C_5H_4N)(C_{10}H_7N_2)(CO)_5]$ from a dichloromethane solution layered with methanol (Found: C, 41.6; H, 1.9; N, 6.8. $C_{20}H_{11}N_3O_5Ru_2$ calc.: C, 41.7; H, 1.9; N, 7.3%).

7 Structure of **2**. Red crystal, $C_{20}H_{11}N_3O_5Ru_2$, $M = 575.48$ g mol^{-1}, size $= 0.28 \times 0.16 \times 0.06$ mm^3, monoclinic, $C2/c$, $a = 24.456(9)$, $b = 11.791(5)$, $c = 14.113(4)$ Å, $\beta = 100.65(3)°$, $V = 3999(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.91$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 15.17$ cm^{-1}, $F(000) = 2240$. Nicolet R3v/m diffractometer, Mo-radiation ($\lambda = 0.71073$ Å), room temperature data corrected empirically for absorption. Direct methods, $R = 0.0638$, $R' = 0.0595$, where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F) + 0.000316F^2]$, 131 parameters and 1843 data with $I_o > 3\sigma(I_o)$ in the range $5 \leq 2\theta \leq 50°$. Ruthenium atoms anisotropic with H-atoms included in idealised positions (C–H 0.96 Å, $U = 0.08$ Å^2). Equivalent isotropic thermal parameters for N(3) and C(21) are 0.038 and 0.046 Å^2 but if N(3) is refined as a carbon atom and C(21) as a nitrogen atom their respective thermal parameters become 0.023 and 0.094. The orientation of the 2-pyr ligand in Fig. 1 is therefore probably correct. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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