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Research paper

Ruthenium carbonyl complexes bearing bidentate pyridine-alkoxide ligands: Synthesis, crystal structures and reactivity

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ABSTRACT

The reactions of pyridine alcohols $PyCH_2CH(Ar)OH$ [Ar = Ph (**1**), 4-$CH_3C_6H_4$ (**2**), 4-ClC_6H_4 (**3**)], and $PyCH_2C(CH_3)_2OH$ (**4**) with $Ru_3(CO)_{12}$ in refluxing toluene gave a series of ruthenium carbonyl complexes PyCH = C(Ph)O][PyCH = C(Ph))$Ru(CO)_2$ (**5**) and $[PyCH_2CH(Ph)O]_2Ru_3(CO)_8$ (**6**), [PyCH = C(4-$CH_3C_6H_4$)O]$_2Ru_3(CO)_8$ (**7**), $[PyCH_2CH(4\text{-}ClC_6H_4)O]_2Ru_3(CO)_8$ (**8**) and $[PyCH_2C(CH_3)_2O]Ru_3(CO)_8$ (**9**) respectively. Five new complexes **5–9** were characterized by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectroscopy. The crystal structures of complexes **5–8** were determined by X-ray crystal diffraction analysis. Moreover, the reactivity of complex **6** had been investigated, when **6** was treated with cyclopentadiene in refluxing toluene, dinuclear metal carbonyl complexes $[(\eta^5\text{-}C_5H_5)Ru(CO)]_2(\mu\text{-}CO)_2$ (**10**) was obtained. Similar treatment of **6** with indene gave the product $[(\eta^5\text{-}C_9H_7)Ru(CO)]_2(\mu\text{-}CO)_2$ (**11**).

1. Introduction

The coordination chemistry of nitrogen donor ligands has been extensively studied and is mostly related to their relevance to biological systems [1]. Transition metal complexes of nitrogen-containing heterocyclic compounds such as pyridine, di- and poly-pyridine, azines and their derivatives are also of great interest due to their ability to undergo facile electrochemical processes. Furthermore, their abilities to absorb visible light to act as electron reservoirs are promising factors in their applications as photosensitizers [2,3]. On the other hand, transition metal carbonyl complexes are very interesting for their reactivity in catalytic reactions such as hydrogenation, hydroformylation and carbonylation [4–8]. Moreover, metal carbonyl derivatives of nitrogen donor ligands are important routes to prepare interesting metal carbonyl complexes [9,10]. In our earlier communications, we reported the behaviour of several mono-dentate nitrogen donor ligands with $Ru_3(CO)_{12}$ [11–15]. Our interest in investigation of the reaction of $Ru_3(CO)_{12}$ with several nitrogen and oxygen donor ligands has prompted us to investigate the reactions of $Ru_3(CO)_{12}$ with some pyridine derivatives. Here we describe the preparation and characterization of some new ruthenium carbonyl derivatives containing bidentate pyridine-alkoxide ligands.

2. Experimental

2.1. General considerations

Schlenk and vacuum-line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under an argon dry atmosphere. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 500 or Bruker Av III-600 instrument in $CDCl_3$, while IR spectra were recorded as KBr disks on a FT IR 8900 spectrometer. Elemental analyses were performed with a VarioEL III analyzer. The different functional groups pyridine-containing alcohol ligands $PyCH_2CH(Ar)OH$ [Ar = Ph (**1**), 4-$CH_3C_6H_4$ (**2**), 4-Cl C_6H_4 (**3**)], and $PyCH_2C(CH_3)_2OH$ (**4**) were prepared by literature methods [16,17].

2.2. Synthesis of complexes [PyCH = C(Ph)O][PyCH = C(Ph))$Ru(CO)_2$ (5) and $[PyCH_2CH(Ph)O]_2Ru_3(CO)_8$ (6)

A solution of ligand precursor $PyCH_2CH(Ph)OH$ (**1**) (0.190 g, 0.938 mmol) and $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) in toluene (30 mL) was refluxed for 6 h. After removal of solvent, the residue was chromatographed on an alumina column using petroleum ether/ethyl acetate as eluent. The first band (red) afforded **5** (0.080 g, 18.5% yield) as orange-red crystals. The second band (red) gave **6** (0.184 g, 42.5% yield) as orange-red crystals.

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For **5**: M.p. 116.7 °C. Anal. Calcd. for $C_{28}H_{20}N_2O_3Ru$: C, 63.03; H, 3.78; N, 5.25. Found: C, 63.10; H, 3.85; N, 5.30. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, 1H, J = 8.0 Hz, Py-H), 7.66–7.68 (m, 2H, Py-H), 7.57–7.61 (m, 2H, Py-H), 7.49–7.53 (m, 3H, Ph-H), 7.37 (t, 2H, J = 9.5 Hz, Py-H), 7.29–7.31 (m, 1H, Py-H), 7.23–7.26 (m, 4H, Ph-H), 7.01 (s, 1H, J = 10.5 Hz, Ph-H), 6.87 (s, 1H, −CH═CH−), 6.73–6.80 (m, 2H, Ph-H), 5.74 (s, 1H, −CH═CH−); ^{13}C NMR(125 MHz, $CDCl_3$): 94.1, 116.5, 118.8, 121.4, 123.9, 125.7, 126.4, 126.6, 127.8, 128.0, 128.5, 131.1, 136.5, 138.3, 141.1, 147.5, 151.7, 154.1, 158.2, 167.1, 169.3, 195.0, 197.0, 199.7. IR (υ_{CO}, KBr, cm^{-1}): 2029(s), 1948(s).

For **6**: M.p. 192.3 °C. Anal. Calcd. for $C_{34}H_{24}N_2O_{10}Ru_3$: C, 44.20; H, 2.62; N, 3.03. Found: C, 44.28; H, 2.70; 3.13. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (t, 2H, J = 1.5 Hz, Py-H), 7.31–7.42 (m, 12H, Py-H, Ph-H), 7.03 (d, 2H, J = 7.5 Hz, Ph-H), 6.70 (t, 2H, J = 6.5 Hz, Ph-H), 4.10 (d, 2H, J = 10.0 Hz, −CH−), 3.19–3.24 (m, 2H, −CH_2−), 2.85 (d, 2H, J = 16.0 Hz, −CH_2−); ^{13}C NMR (125 MHz, $CDCl_3$): 51.5, 77.3, 121.5, 124.3, 125.3, 126.3, 127.3, 136.6, 146.4, 154.0, 160.1, 193.2, 202.8, 202.9. IR (υ_{CO}, KBr, cm^{-1}): 2067(s), 2001(s), 1984(s), 1918(s).

2.3. Synthesis of complex [PyCH = C(4-$CH_3C_6H_4$)O]$_2Ru_3(CO)_8$ (7)

Using a procedure similar to that described above, $PyCH_2CH(4\text{-}CH_3C_6H_4)OH$ (**2**) was reacted with $Ru_3(CO)_{12}$ in refluxing toluene for 6 h. After chromatography and elution with petroleum ether/ethyl acetate, [PyCH = C(4-$CH_3C_6H_4$)O]$_2Ru_3(CO)_8$ (**7**) was obtained (0.166 g, 37.3% yield) as orange-red crystals. M.p. 196.4 °C. Anal. Calcd. for $C_{36}H_{24}N_2O_{10}Ru_3$: C, 45.62; H, 2.55; N, 2.96. Found: C, 45.60; H, 2.49; N, 2.89. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.54 (d, 2H, J = 10.0, Py-H), 7.32–7.44 (m, 4H, Py-H), 7.22 (d, 4H, J = 8.0, Ph-H), 7.05 (d, 4H, J = 8.0, Ph-H), 6.94–7.00 (m, 2H, Py-H), 6.86 (d, 2H, J = 8.5 Hz, −CH═CH−), 2.39 (s, 6H, −CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 14.1, 21.2, 21.4, 21.5, 22.7, 29.4, 29.7, 31.6, 31.9, 52.0, 100.9, 101.8, 118.5, 125.4, 125.6, 125.7, 126.8, 127.9, 128.9, 129.0, 129.1, 136.2, 137.4, 138.1, 138.7, 153.9, 154.5, 154.8, 154.9, 161.3, 165.5, 167.1, 193.7, 204.0, 204.5, 204.6. IR (υ_{CO}, KBr, cm^{-1}): 2067(s), 1990(s), 1915(s).

2.4. Synthesis of complex [$PyCH_2CH(4\text{-}ClC_6H_4)O]_2Ru_3(CO)_8$ (8)

Using a procedure similar to that described above, $PyCH_2CH(4\text{-}ClC_6H_4)OH$ (**3**) was reacted with $Ru_3(CO)_{12}$ in refluxing toluene for 6 h. After chromatography and elution with petroleum ether/ethyl acetate, [$PyCH_2CH(4\text{-}ClC_6H_4)O]_2Ru_3(CO)_8$ (**8**) was obtained (0.157 g, 33.7% yield) as orange-red crystals. M.p. 199.8 °C. Anal. Calcd. for $C_{34}H_{22}Cl_2N_2O_{10}Ru_3$: C, 41.14; H, 2.23; N, 2.82. Found: C, 41.21; H, 2.29; N, 2.90.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, 2H, J = 8.5 Hz, Py-H), 7.50–7.54 (m, 2H, Py-H), 7.41–7.47 (m, 4H, Py-H), 7.21–7.24 (m, 4H, Ph-H), 7.00 (d, 2H, J = 7.0 Hz, Ph-H), 6.88–6.92 (m, 2H, Ph-H), 5.51 (s, 1H, −CH−), 5.40 (s, 1H, −CH−), 4.31 (t, 1H, J = 6.5 Hz, −CH_2−), 3.04–3.09 (m, 1H, −CH_2−), 2.71 (d, 2H, J = 16.0 Hz, −CH_2−); ^{13}C NMR (125 MHz, $CDCl_3$): 30.6, 51.6, 65.6, 101.7, 102.5, 118.9, 119.2, 122.8, 125.4, 125.7, 126.1, 127.0, 128.1, 128.4, 128.5, 128.6, 128.9, 129.2, 132.5, 134.7, 135.4, 136.6, 136.7, 137.9, 139.6, 145.6, 153.6, 154.4, 154.6, 154.8, 161.0, 164.2, 165.9. IR(υ_{CO}, KBr, cm^{-1}): 2068(s), 2013(s), 2001(s), 1974(s), 1929(s).

2.5. Synthesis of complex [$PyCH_2C(CH_3)_2O]Ru_3(CO)_8$ (9)

Using a procedure similar to that described above, $PyCH_2C(CH_3)_2OH$ (**4**) was reacted with $Ru_3(CO)_{12}$ in refluxing toluene for 6 h. After chromatography and elution with petroleum ether/ethyl acetate, [$PyCH_2C(CH_3)_2O]Ru_3(CO)_8$ (**9**) was obtained (0.214 g, 53.9% yield) as orange-red solid. M.p. 183.7 °C. Anal. Calcd. for $C_{28}H_{24}N_2O_{10}Ru_3$: C, 39.49; H, 2.84; N, 3.29. Found: C, 39.51; H, 2.80; N, 3.32. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.96 (d, 2H, J = 5.5 Hz, Py-H), 7.67 (t, 2H, J = 7.5, Py-H), 7.21 (t, 2H, J = 7.0, Py-H), 7.00 (d, 2H, J = 7.5, Py-H), 2.52–2.59 (m, 4H, −CH_2−), 1.26 (s, 6H, −CH_3), 1.17 (s, 6H, −CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): 100.4, 101.3, 117.5, 117.8, 121.5, 124.1, 124.6, 124.9, 125.8, 126.9, 127.3, 127.5, 127.7, 135.3, 136.5, 139.9, 140.1, 146.1, 152.7, 153.4, 153.7, 153.8, 160.2, 164.3, 166.0, 192.5, 193.0. IR (υ_{CO}, KBr, cm^{-1}): 2068(s), 1989(s), 1975(s), 1904(s).

2.6. Reactivity of 6 with cyclopentadiene in toluene

A solution of **6** (0.300 g, 0.325 mmol) and cyclopentadiene (0.043 g, 0.650 mmol) in 30 mL of toluene was refluxed for 24 h. After removal of solvent under reduced pressure, the residue was chromatographed on an alumina column using petroleum ether/ethyl acetate as eluent. The orange-red band was eluted and collected. After vacuum removal of the solvents from the above eluate, the residue was recrystallized from *n*-hexane/CH_2Cl_2 at room temperature to give compound **10** as orange-red crystals (yield: 0.080 g, 18.6%). ^{1}H NMR (600 MHz, $CDCl_3$): 5.28 (s, 8H, C_5H_5), 3.49 (s, 2H, C_5H_5); ^{13}C NMR (150 MHz, $CDCl_3$): δ 89.3, 217.4.

2.7. Reactivity of 6 with indene in toluene

Using a procedure similar to that described above, reaction of **6** with indene gave **11** in 20.3% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22–7.24 (m, 4H, C_9H_7), 7.13–7.15 (m, 4H, C_9H_7), 5.56 (d, 4H, J = 2.4 Hz, C_9H_7), 5.50 (t, 2H, J = 2.4 Hz, C_9H_7); ^{13}C NMR (150 MHz, $CDCl_3$): δ 78.6, 96.7, 109.9, 120.0, 125.8.

2.8. Crystallographic studies

Crystals of complexes **5–8** suitable for X-ray diffraction were isolated from the slow evaporation of hexane-dichloromethane solution. Data collection were performed on a Bruker AXS SMART 1000 CCD diffractometer, using graphite monochromated Mo *Kα* radiation (φ/ω scan, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using the SHELXL-97 program system [18]. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions riding on the parent atoms and refined with fixed thermal parameters. Crystallographic data and experimental details of the structure determinations are given in Table 1. The selected bond lengths and bond angles are given in Table 2. CCDC: 1437151, 1437149, 1437153, and 1437154 for **5–8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk of www: http://www.ccdc.cam.ac.uk.

3. Results and discussion

3.1. Reactions of ligand precursors $PyCH_2CH(Ar)OH$ [Ar = Ph (1), 4-$CH_3C_6H_4$ (2), 4-ClC_6H_4 (3)], and $PyCH_2C(CH_3)_2OH$ (4) with $Ru_3(CO)_{12}$ in toluene

When organic ligand $PyCH_2CH(Ph)OH$ (**1**) was treated with $Ru_3(CO)_{12}$ in refluxing toluene for 6 h, the mononuclear product [PyCH = C(Ph)O][PyCH = C(Ph))Ru$(CO)_2$ (**5**) and the triruthenium cluster [$PyCH_2CH(Ph)O]_2Ru_3(CO)_8$ (**6**) were obtained (Scheme 1).

The IR spectrum of **5** shows only two terminal carbonyl absorption at 2029 and 1948 cm^{-1}. The ^{1}H NMR spectrum of **5** shows five groups of peaks for the pyridyl protons at 8.50, 7.66–7.68, 7.57–7.61, 7.37, and 7.29–7.31 ppm, four groups of peaks for the phenyl protons at 7.49–7.59, 7.23–7.26, 7.01, and 6.73–6.80 ppm, and two singlets for the C═C double bond protons at 6.87 and 5.74 ppm, respectively. X-ray diffraction analysis shows that **5** is a mononuclear ruthenium complex,