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Journal of Organometallic Chemistry 650 (2002) 268–273

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Reactions of the cationic diruthenium carbonyl complex $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]^+$ with bidentate ligands; intramolecularly assisted stereospecific synthesis via the second-sphere face-to-face $\pi-\pi$ stacking interactions

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Received 19 November 2001; received in revised form 21 January 2002; accepted 24 January 2002

Abstract

The reactions of the diruthenium carbonyl complexes $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]X$ ($X = BF_4^-$ (**1a**) or PF_6^- (**1b**)) with neutral or anionic bidentate ligands (L,L) afford a series of the diruthenium bridging carbonyl complexes $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-}(L,L))_2]X_n$ ((L,L) = acetate (O_2CMe), 2,2′-bipyridine (bpy), acetylacetonate (acac), 8-quinolinolate (quin); $n = 0$, 1, 2). Apparently with coordination of the bidentate ligands, the bound acetate ligand of $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]^+$ either migrates within the same complex or into a different one, or is simply replaced. The reaction of $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]^+$ (**1**) with 2,2′-bipyridine produces $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-}O_2CMe)_2]$ (**2**), $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-bpy})]^+$ (**3**), and $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-bpy})_2]^{2+}$ (**4**). Alternatively compound **2** can be prepared from the reaction of **1a** with $MeCO_2H-Et_3N$, while compound **4** can be obtained from the reaction of **3** with bpy. The reaction of **1b** with acetylacetone–Et_3N produces $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-acac})]$ (**5**) and $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-acac})_2]$ (**6**). Compound **2** can also react with acetylacetone–Et_3N to produce **6**. Surprisingly $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-quin})_2]$ (**7**) was obtained stereospecifically as the only one product from the reaction of **1b** with 8-quinolinol–Et_3N. The structure of **7** has been established by X-ray crystallography and found to adopt a *cis* geometry. Further, the stereospecific reaction is probably caused by the second-sphere $\pi-\pi$ face-to-face stacking interactions between the phenyl rings of dppm and the electron-deficient six-membered ring moiety of the bound quinolinate (i.e. the N-included six-membered ring) in **7**. The presence of such interactions is indeed supported by an observed charge-transfer band in a UV–vis spectrum. © 2002 Published by Elsevier Science B.V.

Keywords: Ruthenium; Carbonyl; Acetate; 2,2′-Bipyridine; Acetylacetonate; 8-Quinolinolate

1. Introduction

Our recent interest in exploring the novel reactions and structures of diruthenium carbonyl complexes $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]X$ ($X^- = BF_4^-$ (**1a**), PF_6^- (**1b**)) has led us to find that a uni-negative anion (Y^-) such as I^- or N_3^- can convert **1a** into neutral complexes with the acetate ligand removed, $[Ru_2(\mu\text{-dppm})_2(CO)_2(\mu\text{-Y})(\mu\text{-CO)Y}]$, while a neutral PR_3 converts **1a** into the CH_2–P–bond cleaved products with the acetate ligand intact, $[Ru_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(\mu,\eta^2\text{-}O_2CMe)(\eta^2\text{-}CH_2PPh_2)(PR_3)(CO)_2]X$ and $[Ru_2(\mu\text{-dppm})(\mu\text{-}PPh_2)(\mu,\eta^2\text{-}O_2CMe)(PR_3)_2(CO)_2]X$ [1,2]. However, we wish to present here that the reactions of the cation $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]^+$ (**1**) with various anionic or neutral bidentate ligands (L,L) afford a series of diruthenium bridging carbonyl complexes $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-}(L,L))_2]^{n+}$ ((L,L) = acetate (O_2CMe), 2,2′-bipyridine (bpy), acetylacetonate (acac), 8-quinolinolate (quin); $n = 0$, 1, 2). Apparently with coordination of the bidentate ligands, the acetate ligand of **1** either migrates intra- or intermolecularly, or is simply replaced to form the observed products. Surprisingly we observed a stereospecific reaction between **1** and 8-quinolate to form $[Ru_2(\mu\text{-dppm})_2(\mu\text{-}CO)_2(\eta^2\text{-quin})_2]$ in the *cis*- rather than *trans*-geometry. Both spectral and structural evidences accumulated for this

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0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01198-1

reaction product indicate obviously that the specific reaction is assisted by the intramolecular second-sphere effect [3].

2. Experimental

The compounds $[Ru_2(CO)_4(\mu\text{-dppm})_2(\mu,\eta^2\text{-}O_2CMe)]X$ ($X^- = BF_4^-$ (**1a**), PF_6^- (**1b**)) [4] were prepared according to the literature method. All reactions were performed under prepurified nitrogen using freshly distilled solvents. ^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker AMC400 spectrometer (^{1}H, 400 MHz; ^{31}P, 162 MHz) calibrated against internal deuterated solvents (^{1}H) or external 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Bio-Rad FTS 175 instrument. UV–vis spectra were carried out on a Hewlett–Packard HP8452A instrument. Microanalyses were carried out by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

2.1. Reaction between $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]X$ and 2,2′-bipyridine

2.1.1. Method A

In a 100 ml Schlenk flask were added 0.696 g of **1a** (0.566 mmol), 0.132 g of bpy (0.837 mmol), and 20 ml of MeCN at room temperature. The mixture was then heated at 82 °C for 8.5 h forming yellow precipitate and orange–red solution. The precipitate was collected on a medium frit, washed six times with 5 ml of MeCN, and dried under vacuum to afford 0.042 g of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**). Yield 6%. The filtrate was combined and the solvent was removed under vacuum forming a solid residue. Recrystallization from CH_2Cl_2–MeOH gave 0.635 g of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-bpy})][BF_4]$ (**3a**). Yield 84%. **2**, Anal. Calc. for $C_{56}H_{50}O_6P_4Ru_2$: C, 58.74; H, 4.40. Found: C, 58.68; H, 4.41%. ^{1}H-NMR (CD_2Cl_2): δ 0.70 (s, 6H, Me), 2.66 (s, 4H, $Ph_2PCH_2PPh_2$), 7.17–7.47 (m, 40H, $Ph_2PCH_2PPh_2$). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 35.62 (s, 4 P). IR (CH_2Cl_2): ν(CO), 1669 (s) cm^{-1}. **3a**, Anal. Calc. for $C_{64}H_{55}BF_4N_2O_4P_4Ru_2$: C, 57.84; H, 4.17; N, 2.11. Found: C, 57.47; H, 4.19; N, 2.08%. ^{1}H-NMR (CD_2Cl_2): δ 0.64 (s, 3H, Me), 2.61 (s, 4H, $Ph_2PCH_2PPh_2$), 6.68–7.43 (m, 40H, $Ph_2PCH_2PPh_2$), and bpy signals at δ 7.06 (m, 2H), 7.53 (m, 2H), 7,63 (d, 2H, $^3J_{H,H} = 7.9$ Hz), 9.95 (d, 2H, $^3J_{H,H} = 5.2$ Hz). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 28.71 (m, 2 P), 31.19 (m, 2 P). IR (CH_2Cl_2): ν(CO), 1659 (s) cm^{-1}.

2.1.2. Method B

In a 100 ml Schlenk flask were added 0.389 g of **1b** (0.302 mmol), 0.064 g of bpy (0.406 mmol), and 24 ml of MeCN at room temperature. The mixture was then heated at 82 °C for 13 h forming yellow precipitate and orange–red solution. The precipitate was collected on a medium frit, washed twice with 5 ml of MeCN, and dried under vacuum to afford 0.011 g of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**). Yield 3%. The filtrate was combined and 0.112 g of NH_4PF_6 (ca. 0.69 mmol)) was added. The solvent was then removed from the mixture under vacuum forming a solid residue. Recrystallization from CH_2Cl_2–MeOH gave 0.342 g of impure $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})(\eta^2\text{-}O_2CMe)][PF_6]$ (**3b**), contaminated with $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2][PF_6]_2$ (**4b**) in a ratio of **3b**/**4b** = 18/1 based on the ^{1}H-NMR signals.

2.2. Preparation of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**)

In a 100 ml Schlenk flask were added 0.202 g of **1b** (0.157 mmol), 1.5 ml of acetic acid (ca. 26 mmol), 1.5 ml of Et_3N (ca. 11 mmol), and 24 ml of MeCN at room temperature. The mixture was then heated at 82 °C for 7 h forming yellow precipitate. The precipitate was collected on a medium frit, washed twice with 10 ml of MeCN, and dried under vacuum to afford 0.120 g of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**). Yield 67%.

2.3. Preparation of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2][PF_6]_2$ (**4b**)

In a 100 ml Schlenk flask were added 0.202 g of impure **3b** described above, 0.073 g of bpy (0.463 mmol), and 20 ml of MeCN at room temperature. The mixture was then heated at 82 °C for 90 h. 0.237 g of NH_4PF_6 (ca. 1.381 mmol) was added, and the volume of the solution was then reduced to ca. 1 ml. 10 ml of MeOH was added and the resulting suspension was filtered through a medium frit. The orange–yellow solid was washed with 5 ml of MeOH, and 5 ml of CH_2Cl_2, and dried under vacuum to give 0.122 g of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2][PF_6]_2$ (**4b**). Anal. Calc. for $C_{72}H_{60}F_{12}N_4O_2P_6Ru_2$: C, 53.08; H, 3.71; N, 3.44. Found: C, 52.85; H, 3.69; N, 3.37%. ^{1}H-NMR (CD_2Cl_2): δ 3.29 (s, 4H, $Ph_2PCH_2PPh_2$), 7.22–8.99 (m, 40H for $Ph_2PCH_2PPh_2$ and 8H for bpy), and bpy signals at δ 9.32 (d, 4H, $^3J_{H,H} = 5.1$ Hz), 10.93 (d, 2H, $^3J_{H,H} = 5.3$ Hz). ^{31}P{^{1}H}-NMR (CD_3CN): δ 23.00 (s, 4 P). IR (CH_2Cl_2): ν(CO), 1655 (s) cm^{-1}.

2.4. Reaction between $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)][PF_6]$ (**1b**) and acetylacetone–Et_3N

In a 100 ml Schlenk flask were added 0.149 g of **1b** (0.116 mmol), 0.6 ml of acetylacetone (ca. 5.84 mmol), 2 ml of Et_3N (ca. 14.3 mmol) and 20 ml of CH_2Cl_2 at room temperature. The mixture was then heated at 40 °C for 24.5 h. The volatiles were removed under vac-

uum. Recrystallization from CH_2Cl_2–MeOH gave 0.089 g of a pink solid. The volume of the filtrate obtained from recrystallization was reduced to ca. 2 ml, forming 0.006 g of an orange–yellow solid. This solid was collected and found to be $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-acac})]$ (**5**). Yield 4%. The pink solid was found to be $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-acac})_2]$ (**6**). Yield 63%. **5**, Anal. Calc. for $C_{59}H_{54}O_6P_4Ru_2$: C, 59.80; H, 4.59. Found: C, 59.47; H, 4.89. ^{1}H-NMR ($CDCl_3$): δ 0.85 (s, 3 H, *Me*CO_2), 0.91 (s, 6 H, *Me* of acac), 2.56 (s, 4 H, $Ph_2PCH_2PPh_2$), 4.11 (s, 1 H, *H* of acac), 7.12–7.56 (m, 40 H, *Ph*$_2$PCH$_2$P*Ph*$_2$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 31.77 (m, 2 P), 33.00 (m, 2 P). IR (CH_2Cl_2): ν(CO), 1690 (s) cm^{-1}. **6**, Anal. Calc. for $C_{62}H_{58}O_6P_4Ru_2$: C, 60.78; H, 4.77. Found: C, 60.53; H, 4.95%. ^{1}H-NMR (CD_2Cl_2): δ 0.94 (s, 12H, *Me* of acac), 2.48 (s, 4H, $Ph_2PCH_2PPh_2$), 4.12 (s, 2H, *H* of acac), 7.07–7.48 (m, 40H, *Ph*$_2$PCH$_2$P*Ph*$_2$). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 30.71 (s, 4 P). IR (CH_2Cl_2): ν(CO), 1656 (s) cm^{-1}. UV–vis (CH_2Cl_2): 232 ($\varepsilon = 850$), 256 (710), 308 (240) nm.

Table 1
Crystal data

Compound	**7**·3CH_2Cl_2
Empirical formula	$C_{73}H_{62}Cl_6IN_2O_4P_4Ru_2$
Formula weight	1569.97
Space group	Triclinic, $P\bar{1}$
a (Å)	14.2282(2)
b (Å)	14.6067(2)
c (Å)	18.8527(2)
α (°)	79.716(1)
β (°)	87.126(1)
γ (°)	62.927(1)
V (Å^3)	3506.6(6)
Z	2
D_{calc} (g cm^{-3})	1.520
F(000)	1592
Unit cell detn	
2θ range (°)	2–53
h, k, l range	±17, ±18, ±23
μ(Mo–K$_\alpha$) (mm^{-1})	0.818
Transmission factors	0.8621–0.6547
λ (Mo–K$_\alpha$) (Å)	0.71073
Crystal size (mm)	0.20 × 0.14 × 0.12
Temperature (K)	150(1)
Number of measured reflections	29 516
Number of observed reflections (N_o)	13586 ($>2\sigma$)
R [a], R_w [a]	0.0675, 0.1714
Goodness-of-fit [a]	1.070
Refinement program	NRCVAX
Number of refined parameters (N_p)	816
Weighting scheme	$[\sigma^2(F_o)+0.0013F_o^2]^{-1}$
$(\Delta\rho)_{max}$ (e Å^3)	2.427
$(\Delta\rho)_{min}$ (e Å^3)	−1.275

[a] $R = [\Sigma||F_o|-|F_c||/\Sigma|F_o|]$. $R_w = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. GOF $= [\Sigma\omega(|F_o|-|F_c|)^2/N_o-N_p]]^{1/2}$.

2.5. Preparation of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-acac})_2]$ (6)

In a 100 ml Schlenk flask were added 0.103 g of **2** (0.090 mmol), 2 ml of acetylacetone (ca. 19.5 mmol), 2 ml of Et_3N (ca. 14.3 mmol) and 20 ml of CH_2Cl_2 at room temperature. The mixture was then stirred for 16 h. The volatiles were removed under vacuum. Recrystallization from CH_2Cl_2–MeOH gave 0.091 g of a pink solid, **6**. Yield 82%.

2.6. Preparation of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-quin})_2][PF_6]_2$ (7)

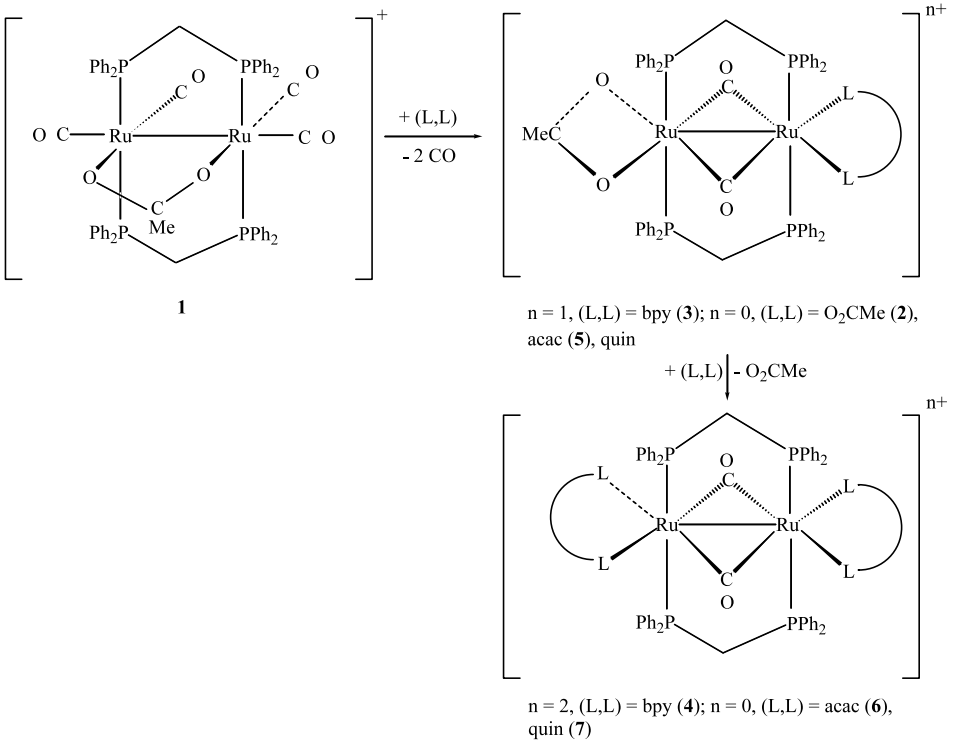
In a 100 ml Schlenk flask were added 0.198 g of **1b** (0.154 mmol), 0.069 g of 8-quinolinol (0.471 mmol), 2 ml of Et_3N (ca. 14.3 mmol), and 21 ml of CH_2Cl_2 at room temperature. The mixture was then heated at 40 °C for 22 h. The solvent was removed under vacuum. Recrystallization from CH_2Cl_2–MeOH gave 0.150 g of orange–yellow $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-quin})_2]$ (**7**). Yield 74%. Anal. Calc. for $C_{70}H_{56}N_2O_4P_4Ru_2$: C, 63.92; H, 4.29; N, 2.13. Found: C, 63.76; H, 4.28; N, 2.11%. ^{1}H-NMR (CD_2Cl_2): δ 2.51 (m, $Ph_2PCH_2PPh_2$, 2H), 2.20 (m, $Ph_2PCH_2PPh_2$, 2H), 6.10–9.10 (m, *Ph* and quin, 52H). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ 25.06 (s, 4 P). IR (CH_2Cl_2): ν(CO), 1734s cm^{-1}. UV–vis (CH_2Cl_2): 234 ($\varepsilon = 1100$), 260 (1100), 356 (140), 458 (120) nm.

2.7. X-ray data collection, solution and refinement

Data were collected at 150 K on a Siemens SMART-CCD instrument, equipped with a normal focus and 3 kW sealed-tube X-ray source. The structures of **7** were solved by heavy-atom methods and refined by a full-matrix least-squares procedure using NRCVAX [5]. All the non-hydrogen atoms were refined anisotropically. The other essential details of single-crystal data measurement and refinement are given in Table 1. Three CH_2Cl_2 molecules were found in the asymmetric unit of the crystal of **7**. There is a residual peak with 2.427 e Å^{-3} in a distance of 1.037 Å close to the Ru(2) atom on the last difference Fourier map.

3. Results and discussion

The reaction of $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]^+$ (**1**) with 2,2′-bipyridine (bpy) in a slightly excess amount, relative to that of **1**, produces $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**), $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})(\eta^2\text{-}O_2CMe)]^+$ (**3**), and $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2]^{2+}$ (**4**). Compound **3** is the major product. The neutral compound, **2**, is insoluble in the reaction solvent, MeCN, and can be separated from other products, **3** and **4**. However, we had difficulty



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Scheme 1.

separating the mixture of $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})(\eta^2\text{-}O_2CMe)][PF_6]$ (**3b**) and $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2][PF_6]_2$ (**4b**), when $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)][PF_6]$ (**1b**) was used as the reactant. Fortunately we soon found that $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2][BF_4]_2$ (**4a**) is slightly soluble in MeOH but not in CH_2Cl_2. Hence, we start the reaction using $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)][BF_4]$ (**1a**) as the reactant, and then with a simple recrystallization from CH_2Cl_2–MeOH, we can obtain $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})(\eta^2\text{-}O_2CMe)][BF_4]$ (**3a**) as a pure solid.

Alternatively, compound **2** can be prepared from the reaction of **1a** with $MeCO_2H$–Et_3N, while the pure compound, **4b**, can be obtained from the reaction of the impure **3b**, contaminated with **4b** in a ratio of **3b**/**4b** = 18/1 based on the ^{1}H-NMR signals. Thus, it appears that with the coordination of a neutral bidentate ligand such as bpy, the bound acetate ligand in **1** can migrate intramolecularly to form **3** first, then replaced subsequently by a second bpy to form **4**. The replaced acetate finds **1** in the reaction solvent, MeCN, and reacts to form the insoluble precipitate, **2** (Scheme 1).

The reaction of **1b** with acetylacetonate (acac), via acetylacetone–Et_3N, in CH_2Cl_2 produces $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-acac})]$ (**5**) and $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-acac})_2]$ (**6**). The solubility of both compounds is different in two organic solvents used. Compound **6** is insoluble in MeOH but slightly soluble in CH_2Cl_2. Compound **5** is very soluble in this solvent but slightly soluble in MeOH. Hence, compounds **5** and **6** can be separated easily. Compound **6** obtained from the reaction is the major product, while compound **5** is the minor one. When the reaction time is lengthened from 24.5 h to more than 30 h, compound **6** can be obtained as a pure product. Compound **6** can also be prepared via an alternative way from the reaction of **2** with acetylacetone–Et_3N. Apparently the reaction of **1b** with an anionic bidentate ligand such as acetylacetonate follows a similar pathway to that of **1** with bpy. It forms **5** first, and then **6**. The neutral product, **2**, if obtained as one of the products, is soluble in the reaction solvent, CH_2Cl_2, and reacts further with acetylacetonate to form **6** as the final product. Likewise the reaction of **1b** with 8-quinolinolate (quin) via 8-quinolinol/Et_3N may form $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-quin})]$ first, and then $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-quin})_2]$ (**7**) (Scheme 1).

The four P atoms resonate in the $^{31}P\{^1H\}$-NMR spectra as one singlet at δ 35.62 for $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**), 23.00 for $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-bpy})_2]^{2+}$ (**4**), and 30.71 for $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-acac})_2]$ (**6**), indicating that the molecule may adopt a geometry with a D_{2h} symmetry. Since 8-quniolate is an anionic (O, N) bidentate ligand, we expected to obtain a mixture of both *cis*- and *trans*-$[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-quin})_2]$ with the former in a C_{2v} symmetry and the latter in a C_{2h} symmetry before the experiment. To our surprise, the reaction appears quite

stereospecific to produce only one product **7**, showing only one $^{31}P\{^{1}H\}$ singlet at δ 25.06. In order to find out the specific geometry and the possible cause, the solid-state structure of **7** was determined by X-ray crystallography. The two (O, N) ligands were found to adopt the *cis* rather than *trans* geometry (Fig. 1). In a projection view with overlapping P(1) and P(3) atoms (and overlapping P(2) and P(4) atoms) (Fig. 2), we found that some sort of π–π face-to-face stacking interactions probably exist between the phenyl rings of dppm above or below the electron-deficient six-membered ring moiety of the quinolinate (i.e. the N-included six-membered ring plane). The distances and angles formed between two such nearly parallel planes are (3.531 Å, 15.90°) between plane 1 and plane 2, (3.569 Å, 20.69°) between plane 2 and plane 3, (3.599 Å, 19.8°) between plane 4 and plane 5, and (3.636 Å, 22.62°) between plane 5 and plane 6, where plane 1 contains C23, C24, C25, C26, C27, and C28; plane 2 contains N1, C3, C4, C5, C6, and C11; plane 3 contains C53, C54, C55, C56, C57, and C58; plane 4 contains C41, C42, C43, C44, C45, and C46; plane 5 contains N2, C12, C13, C14, C15, and C20; and plane 6 contains C65, C66, C67, C68, C69, and C70. This "second-sphere coordination" via the π–π interactions may help to drive a stereospecific reaction between **1b** and 8-quinolate [3,6]. Indeed, the presence of such interactions is supported by an observed charge-transfer band at 458 nm in a UV–vis spectrum measured in CH_2Cl_2. (Compound **7** also displays three other bands at 234, 260, and 356 nm, but compound **6** displays only three bands at 232, 256, and 308 nm.) This feature reflects apparently that (1) the parallel arrangement and close contact (3.53–3.64 Å) between the phenyl planes of dppm and the N-included six-membered ring planes of quinolate ligands observed in the solid state are also retained in solution, and (2) the quinolate ligand can act as an electron acceptor (a π acid), except for the common role it plays as an electron donor (a σ base) [7]. The π-acid character is probably more important than the σ-base character, for the relatively shorter Ru–Ru distance of 2.7672(6) found in **7**, compared with that of 2.841(1) Å observed in **1b** [3], and for the very high ν(CO) frequency of 1734 cm^{-1} displayed by **7**, compared with that of 1699 in **2**, 1659 in **3**, 1655 in **4**, 1690 in **5**, and 1656 cm^{-1} in **6**.

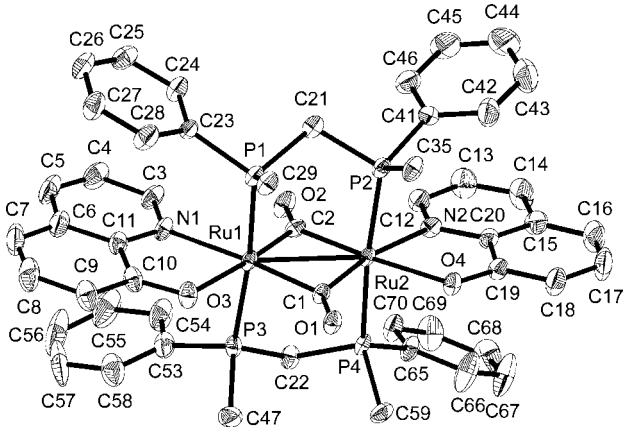

Fig. 1. ORTEP plot of **7** with 50% thermal ellipsoids. Part of phenyl groups containing C(30)–C(34), C(36)–C(40), C(48)–C(52), and C(60)–C(64) atoms are omitted for clarity. Selected bond lengths: Ru(1)–Ru(2) = 2.7676(2), Ru(1)–C(1) = 2.034(6), Ru(1)–C(2) = 1.998(6), Ru(1)–N(1) = 2.182(5), Ru(1)–O(3) = 2.183(4), Ru(1)–P(1) = 2.379(2), Ru(1)–P(3) = 2.367(2), Ru(2)–C(1) = 2.033(6), Ru(2)–C(2) = 1.994(6), Ru(2)–N(2) = 2.188(5), Ru(2)–O(4) = 2.186(4), Ru(2)–P(2) = 2.378(2), Ru(2)–P(4) = 2.367(2), C(1)–O(1) = 1.187(7), C(2)–O(2) = 1.236(7) Å. Selected bond angles: Ru(1)–Ru(2)–C(1) = 47.1(2), Ru(1)–Ru(2)–C(2) = 46.2(2), Ru(2)–Ru(1)–C(1) = 47.1(2), Ru(2)–Ru(1)–C(2) = 46.0(2), Ru(1)–C(1)–Ru(2) = 85.7(2), Ru(1)–C(2)–Ru(2) = 87.8(2), Ru(1)–C(1)–O(1) = 138.0(4), Ru(1)–C(2)–O(2) = 136.3(4), Ru(2)–C(1)–O(1) = 136.3(4), Ru(2)–C(2)–O(2) = 135.7(4), C(1)–Ru(1)–O(3) = 94.4(2), O(3)–Ru(1)–N(1) = 76.1(2), N(1)–Ru(1)–C(2) = 96.5(2), C(2)–Ru(1)–C(1) = 93.1(2), C(1)–Ru(2)–O(4) = 93.6(2), O(4)–Ru(2)–N(2) = 75.7(2), N(2)–Ru(2)–C(2) = 97.5(2), C(2)–Ru(2)–C(1) = 93.3(2), P(1)–Ru(1)–P(3) = 173.74(5), P(2)–Ru(2)–P(4) = 174.66(5)°.

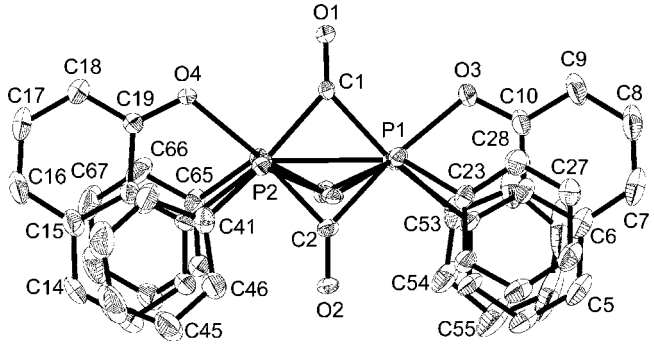

Fig. 2. A projection view of **7** along P(1)→P(3) and P(2)→P(4) vectors. Phenyl groups containing C(29)–C(34), C(35)–C(40), C(47)–C(52), and C(59)–C(64) are omitted for clarity.

4. Conclusion

The reactions of the diruthenium carbonyl cation $[Ru_2(\mu\text{-dppm})_2(CO)_4(\mu,\eta^2\text{-}O_2CMe)]^+$ (**1**) with neutral or anionic bidentate ligands (L,L) afford a series of the diruthenium bridging carbonyl complexes $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-(L,L)})_2]^{n+}$ ((L,L) = acetate (O_2-CMe), 2,2′-bipyridine (bpy), acetylacetonate (acac), 8-quinolinolate (quin); $n = 0$, 1, 2). Apparently with the coordination of a bidentate ligand, the bound acetate ligand in **1** can migrate intramolecularly to form $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)(\eta^2\text{-(L,L)})]^{n+}$ ($n = 0$, (L,L) = acac (**5**), quin; $n = 1$, (L,L) = bpy (**3**)) first, then replaced subsequently by a second (L,L) to form $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-(L,L)})_2]^{n+}$ ($n = 0$, (L,L) = acac (**6**), quin (**7**); $n = 2$, (L,L) = bpy (**4**)). The replaced acetate can react with **1** to form $[Ru_2(\mu\text{-dppm})_2(\mu\text{-CO})_2(\eta^2\text{-}O_2CMe)_2]$ (**2**) as an insoluble precipitate in MeCN. However, if the reaction solvent is CH_2Cl_2, **2**

remains soluble and can react further with two equivalents of (L,L) to produce the substituted product such as **6** (Scheme 1). The crystal structure of **7** was determined by X-ray crystallography to reveal a stereospecific reaction between **1** and quin, forming a *cis*-{$Ru_2(\eta^2\text{-quin})_2$} arrangement (Fig. 1). The possible cause is due to the intramolecular π–π face-to-face stacking interactions between the phenyl rings of dppm above and below the π-electron-deficient N-included six-membered ring plane of the bound quinolinate (Fig. 2). The presence of such interactions is further supported by an observed charge-transfer band in a UV–vis spectrum.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 173958 for compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the National Science Council of the Republic of China for financial support of this research (Contract No. NSC90-2113-M006-021).

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