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Dimeric and polymeric ruthenium complexes with Ru–vinyl linkages

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Abstract

The carbonyl hydrido complex $RuHCl(CO)(PPh_3)_3$ reacted with diynes HC≡C–R–C≡CH (R = *p*-C_6H_4, *p*-C_6H_4–C_6H_4) to give the five-coordinate vinyl ruthenium dimeric compounds $[RuCl(CO)(PPh_3)_2]_2(\mu$-CH=CH–R–CH=CH) in high yields. Additions of 2,6-dimethylphenyl isocyanide (CNC_8H_9) or 4-phenylpyridine (Ph–Py) to the vinyl complexes produced the six-coordinate adducts $[RuCl(CO)(C_8H_9NC)(PPh_3)_2]_2(\mu$-CH=CH–R–CH=CH) and $[RuCl(CO)(Ph–Py)(PPh_3)_2]_2(\mu$-CH=CH–R–CH=CH) respectively. Reactions of $[RuCl(CO)(PPh_3)_2]_2(\mu$-CH=CH–R–CH=CH) with L (L = 2,3,5,6-tetramethylphenyl diisocyanide or 4,4′-bipyridine) produced $[RuCl(CO)(PPh_3)_2(\mu$-CH=CH–R–CH=CH)$RuCl(CO)(PPh_3)_2(\mu$-L)$]_x$. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Vinyl ruthenium compounds; Dimers; Polymers

1. Introduction

There has been increasing interest in the preparation of conjugated metal-containing polymeric organometallic complexes because of their unusual electrical, electrochemical, and optical properties and their potential technological applications (for reviews on conjugated organometallic complexes, see for example Ref. [1]). The most common conjugated organometallic polymers with transition metals in the main chains include polymers with metal acetylide linkages (for recent work on metal acetylide polymers, see for example Ref. [2]) or coordination bonds with diisocyanides [3], stacked polymers [4], and metallocene polymers (see for example Ref. [5]). As many useful conjugated organic materials (for example polyacetylene and poly(phenylene vinylene)) have only sp^2 carbons in their backbones (see for example Ref. [6]), it would be interesting to prepare organometallic polymers with M–C(sp^2) linkages. However, examples of such complexes are still rare; only a few complexes of the type $[ML_n(\mu$-Ar–$)]_x$ have been reported [7].

We have attempted to prepare dimeric and polymeric ruthenium complexes with Ru–vinyl linkages. This article reports the details of the synthesis and characterization of these new compounds. Previously reported dimeric complexes with metal–vinyl linkages include $[(TMP)Ru]_2(\mu$-CH=CH) (TMP = tetramesitylporphyrin) [8], $Cp_2ZrCl(\mu$-CH=CH)$Ru(PPh_3)_2Cp$ [9], $[CpFe(LL')]_2(\mu$-CH=CH–CH=CH) (LL′ = dppm, $(CO)_2$, $(CO)(PMe_3)$, $(CO)(PPh_3)$) [10], $(DME)((CF_3)_2MeCO)_2(ArN)Mo$=CH–CH=CH–CH=CH–CH=$Mo(NAr)(OCMe(CF_3)_2)$-(DME) [11], $(Cp_2ZrCl)_2(\mu$-*p*-CH=CH–C_6H_4–CH=CH) [12], $[RuCl(CO)(PPh_3)(L)]_2(\mu$-*p*-CH=CH–$C_6H_4$–CH=CH) (L = PPh_3 [13], dppf [13]) and a few complexes with μ-CR=CR′ bridges (e.g. $CpRu(CO)_2(\mu$-CR=CR)$Ru(PPh_3)_2Cp$ (R = CO_2Me) and $[(PR_3)Au]_2(\mu$-CF_3C=$CCF_3)$) [14–16].

2. Experimental section

All reactions were carried out under a nitrogen atmosphere using standard Schlenck techniques. Solvents were distilled under nitrogen from sodium–benzophenone (hexane, ether, THF, benzene) or calcium hydride (CH_2Cl_2). Microanalyses were performed by MEDAC Ltd. (Middlesex, UK) or M–H–W Lab. (Phoenix, AZ, USA). ^1H, ^{13}C and ^{31}P NMR spectra were collected on a JEOL EX-400 spectrometer or a Bruker ARX-300 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to TMS, and ^{31}P NMR

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chemical shifts relative to 85% H_3PO_4. IR spectra were collected on a Perkin–Elmer 1600 spectrometer.

$RuHCl(CO)(PPh_3)_3$ [17], $RuHCl(CO)(PCy_3)_2$ [18], $HC{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CH$ [19], $HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$ [19], 2,3,5,6-tetramethylphenyl diisocyanide [20] and $RuCl(CH{=}CHPh)(CO)(PPh_3)_2$ [21] were prepared according to literature methods. All other reagents were used as purchased from Aldrich or Fluka.

2.1. $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}C_6H_4{-}CH{=}CH)$, **2a**

To a suspension of $RuHCl(CO)(PPh_3)_3$ (200 mg, 0.21 mmol) in CH_2Cl_2 (8 ml) at room temperature was added $HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$ (12 mg, 0.095 mmol). The reaction mixture was stirred for 15 min to give a red solution. The volume of the reaction mixture was reduced to 1 ml under vacuum and 15 ml of ether was added to give a red precipitate. The red solid obtained was collected by filtration, washed with ether and hexane and dried under vacuum. Yield 122 mg, 85%. Anal. Found: C, 66.55; H, 4.53. $C_{84}H_{68}Cl_2O_2P_4Ru_2$ Calc.: C, 66.98; H, 4.55%. IR (KBr, cm^{-1}): 1924 vs [ν(C≡O)]. ^1H NMR ($CDCl_3$): δ 8.23 (d, J(HH) = 13.7 Hz; 2 H, Ru–CH), 7.68–7.31 (m, 60 H, 4 PPh_3), 6.54 (s, 4 H, C_6H_4), 5.54 (d, J(HH) = 13.7 Hz, 2 H, =CH). ^{31}P NMR ($CDCl_3$): δ 29.0 (s). ^{13}C NMR ($CDCl_3$): δ 201.4 (t, J(PC) = 14.3 Hz, CO), 144.9 (t, J(PC) = 11.3 Hz, Ru–CH), 135.3 (t, J(PC) = 3.9 Hz, Ru–CH=*CH*), 135.1 (t, J(PC) = 2.1 Hz, *ipso*-C_6H_4), 134.5 (t, J(PC) = 7.5 Hz, *o*-PPh_2), 131.7 (t, J(PC) = 22.0 Hz, *ipso*-PPh_2), 130.0 (s, *p*-PPh_2), 128.2 (t, J(PC) = 4.8 Hz, *m*-PPh_2), 124.2 (s, C_6H_4).

2.2. $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}C_6H_4{-}C_6H_4{-}CH{=}CH)$, **2b**

To a suspension of $RuHCl(CO)(PPh_3)_3$ (200 mg, 0.21 mmol) in CH_2Cl_2 (8 ml) at room temperature was added $HC{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CH$ (19.2 mg, 0.095 mmol). The reaction mixture was stirred for 15 min to give a red solution. The volume of the reaction mixture was reduced to 1 ml under vacuum and 15 ml of ether was added to give a red precipitate. The red solid was collected by filtration, washed with ether and hexane and dried under vacuum. Yield 138 mg, 83%. Anal. Found: C, 68.17; H, 4.76. $C_{90}H_{72}Cl_2O_2P_4Ru_2$ Calc.: C, 68.31; H, 4.59%. IR (KBr, cm^{-1}): 1936 vs [ν(C≡O)]. ^1H NMR ($CDCl_3$): δ 8.46 (d, J(HH) = 13.2 Hz, 2 H, Ru–CH), 7.59–7.32 (m, 64 H, 4 PPh_3, 1/2 C_6H_4–C_6H_4), 6.80 (d, J(HH) = 8.3 Hz, 4 H, 1/2 C_6H_4–C_6H_4), 5.62 (d, J(HH) = 13.2 Hz, 2 H, =CH). ^{31}P NMR ($CDCl_3$): δ 29.8 (s). ^{13}C NMR ($CDCl_3$): δ 201.5 (t, J(PC) = 14.1 Hz, CO), 147.3 (t, J(PC) = 11.1 Hz, Ru–CH), 137.5 (t, J(PC) = 3.9 Hz, *4*-C_6H_4), 136.8 (s, C_6H_4), 135.1 (t, J(PC) = 3.5 Hz, Ru–CH=*CH*), 134.2–124.6 (m, other aromatic signals).

2.3. $[RuCl(CO)(C_8H_9N{\equiv}C)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}C_6H_4{-}CH{=}CH)$, **3a**

To a solution of **2a** (200 mg, 0.133 mmol) in 8 ml CH_2Cl_2 was added 2,6-dimethylphenyl isocyanide (38 mg, 0.29 mmol). The reaction mixture immediately turned to yellow brown and was stirred under nitrogen for 15 min at room temperature. The volume of the reaction mixture was reduced to 1 ml under vacuum. 15 ml of ether was added to the reaction mixture to give a yellowish brown precipitate. The solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried under vacuum. Yield 172 mg, 73%. Anal. Found: C, 68.54; H, 4.81; N, 1.61. $C_{102}H_{86}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 69.26; H, 4.90; N, 1.58%. IR (KBr, cm^{-1}): 2099 vs [ν(C≡N)], 1960 vs [ν(C≡O)]. ^1H NMR ($CDCl_3$): δ 7.71–6.93 (m, 68 H, 2 Ru–CH, 4 PPh_3, 2 C_6H_3), 6.62 (s, 4 H, C_6H_4), 5.83 (d, J(HH) = 17.6 Hz, 2 H, =CH), 2.11 (s, 12 H, 4 CH_3). ^{31}P NMR ($CDCl_3$): δ 24.8 (s).

2.4. $[RuCl(CO)(C_8H_9N{\equiv}C)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}C_6H_4{-}C_6H_4{-}CH{=}CH)$, **3b**

The procedure is analogous to that for **3a**, starting from **2b** (200 mg, 0.126 mmol) and 2,6-dimethylphenyl isocyanide (36 mg, 0.27 mmol). The product is a yellowish brown solid. Yield 198 mg, 85%. Anal. Found: C, 70.11; H, 5.20; N, 2.13. $C_{108}H_{90}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 70.31; H, 4.91; N, 1.51%. IR (KBr, cm^{-1}): 2116 vs [ν(C≡N)], 1954 vs [ν(C≡O)]. ^1H NMR ($CDCl_3$): δ 8.04 (d, J(HH) = 17.9 Hz, 2 H, Ru–CH), 7.73–6.74 (m, 74 H, 4 PPh_3, C_6H_4–C_6H_4, 2 C_6H_3), 5.91 (d, J(HH) = 17.9 Hz, 2 H, =CH), 2.11 (s, 12 H, 4 CH_3). ^{31}P NMR ($CDCl_3$): δ 25.1 (s).

2.5. $[RuCl(CO)(Ph{-}Py)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}C_6H_4{-}CH{=}CH)$, **4a**

To a solution of **2a** (200 mg, 0.133 mmol) in 8 ml CH_2Cl_2 was added 4-phenylpyridine (46 mg, 0.29 mmol). The reaction mixture turned to green and was stirred under nitrogen for 15 min at room temperature. The volume of the mixture was reduced to 1 ml under vacuum. 15 ml of ether was added to give a greenish yellow precipitate. The solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried under vacuum. The product is a yellow solid. Yield 174 mg, 72%. Anal. Found: C, 69.50; H, 4.73; N, 1.53. $C_{106}H_{86}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 70.08; H, 4.77; N, 1.54%. IR (KBr, cm^{-1}): 1937 vs [ν(C≡O)]. ^1H NMR ($CDCl_3$): δ 8.50–6.65 (m, 84 H, 4 PPh_3, 2 $C_{11}H_9N$, 2 Ru–CH=), 5.75 (d, J(HH) = 16.6 Hz, 2 H, =CH). ^{31}P NMR ($CDCl_3$): δ 25.2 (s). ^{13}C NMR ($CDCl_3$): δ 203.4 (t, J(PC) = 14.4 Hz, CO), 154.5 (br, C(α)–Py), 149.9 (t, J(PC) = 13.7 Hz, Ru–CH), 139.0

(s, Ru–CH=*C*H), 147.6–121.3 (m, other aromatic and pyridine signals).

2.6. *[RuCl(CO)(Ph–Py)(PPh$_3$)$_2$]$_2$(μ-CH=CH–C$_6$H$_4$–C$_6$H$_4$–CH=CH), **4b***

The procedure is analogous to that for **4a**, starting from **2b** (200 mg, 0.126 mmol) and 4-phenylpyridine (43 mg, 0.28 mmol). The product is a greenish yellow solid. Yield 188 mg, 79%. Anal. Found: C, 71.22; H, 4.89; N, 1.67. $C_{112}H_{90}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 71.07; H, 4.79; N, 1.48%. IR (KBr, cm^{-1}): 1928 vs [ν(C≡O)]. ^{1}H NMR ($CDCl_3$): δ 8.88 (d, *J*(HH) = 16.6 Hz, 2 H, Ru–CH), 8.55–6.81 (m, 86 H, 4 PPh_3, C_6H_4–C_6H_4, 2 $C_{11}H_9N$), 5.88 (d, 2 H, *J*(HH) = 16.6 Hz, =CH). ^{31}P NMR ($CDCl_3$): δ 27.6 (s). ^{13}C NMR (CD_2Cl_2): δ 203.3 (t, *J*(PC) = 14.3 Hz, CO), 154.3 (t, *J*(PC) = 13.4 Hz, Ru–CH), 153.9 (s, C(α)–Py), 138.0 (s, Ru–CH=*C*H), 147.8–121.6 (m, other aromatic and pyridine signals), 121.6 (s, C(β)–Py).

2.7. *[RuCl(CH=CHPh)(CO)(PPh$_3$)$_2$]$_2$(μ-C≡NC$_{10}$H$_{12}$N≡C), **5***

To a solution of RuCl(CH=CHPh)(CO)(PPh_3)$_2$ (200 mg, 0.253 mmol) in 8 ml CH_2Cl_2 was added 2,3,5,6-tetramethylphenyl diisocyanide (23.3 mg, 0.127 mmol). The reaction mixture turned to orange brown and was stirred under nitrogen for 15 min at room temperature. After that, the volume of the reaction mixture was reduced to 1 ml under vacuum and 15 ml of ether was added to give a pale brown precipitate. The pale brown solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried under vacuum. Yield 173 mg, 68%. Anal. Found: C, 68.83; H, 4.89; N, 1.54. $C_{102}H_{86}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 69.26; H, 4.90; N, 1.58%. IR (KBr, cm^{-1}): 2090 vs [ν(C≡N)], 1964 vs [ν(C≡O)]. ^{1}H NMR ($CDCl_3$): δ 8.05 (d, *J*(HH) = 18.7 Hz, 2 H, Ru–CH), 7.72–6.84 (m, 70 H, 4 PPh_3, 2 Ph), 5.85 (d, *J*(HH) = 18.7 Hz, 2 H, =CH), 1.98 (s, 12 H, 4 CH_3). ^{31}P NMR ($CDCl_3$): δ 26.9 (s).

2.8. *[RuCl(CO)(CH=CHPh)(PPh$_3$)$_2$]$_2$(μ-NC$_5$H$_4$–C$_5$H$_4$N), **6***

To a solution of RuCl(CO)(CH=CHPh)(PPh_3)$_2$ (200 mg, 0.253 mmol) in 8 ml CH_2Cl_2 was added 4,4′-bipyridine (20 mg, 0.13 mmol). The reaction mixture turned to orange and was stirred under nitrogen for 15 min at room temperature. After that, the volume of the reaction mixture was reduced to 1 ml under vacuum and 15 ml of ether was added to give a yellow precipitate. The yellow solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried under vacuum. Yield 144 mg, 65%. Anal. Found: C, 68.25; H, 4.73; N, 1.57. $C_{100}H_{82}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 69.00; H, 4.75; N, 1.61%. IR (KBr, cm^{-1}): 1914 vs [ν(C≡O)]. ^{1}H NMR ($CDCl_3$): δ 8.82 (d, *J*(HH) = 17.0 Hz, 2 H, Ru–CH), 8.61–6.55 (m, 78 H, 4 PPh_3, 2 Ph, bipy), 5.83 (d, *J*(HH) = 17.0 Hz, 2 H, =CH). ^{31}P NMR ($CDCl_3$): δ 27.6 (s).

2.9. *[(μ-C≡N–C$_{10}$H$_{12}$–N≡C)RuCl(CO)(PPh$_3$)$_2$(μ-CH=CH–C$_6$H$_4$–CH=CH)RuCl(CO)(PPh$_3$)$_2$]$_x$, **7a***

To a solution of **2a** (200 mg, 0.133 mmol) in 8 ml CH_2Cl_2 was added 2,3,5,6-tetramethylphenyl diisocyanide (24 mg, 0.13 mmol). The reaction mixture turned to yellow and was stirred under nitrogen for an hour at room temperature to give a greenish yellow solid. The solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried in vacuo. Yield 179 mg, 80%. Anal. Found: C, 67.24; H, 4.72; N, 1.71. $C_{96}H_{80}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 68.20; H, 4.77; N, 1.66%. The sample was probably contaminated with solvents, for example $C_{96}H_{80}Cl_2N_2O_2P_4Ru_2 \cdot 0.3CH_2Cl_2$ Calc.: C, 67.40; H, 4.73; N, 1.63%. IR (KBr, cm^{-1}): 2090 vs [ν(C≡N)], 1950 vs [ν(C≡O)].

2.10. *[(μ-C≡N–C$_{10}$H$_{12}$–N≡C)RuCl(CO)(PPh$_3$)$_2$(μ-CH=CH–C$_6$H$_4$–C$_6$H$_4$–CH=CH)RuCl(CO)(PPh$_3$)$_2$]$_x$, **7b***

The procedure is analogous to that for **7a**, starting from **2b** (200 mg, 0.126 mmol) and 2,3,5,6-tetramethylphenyl diisocyanide (23 mg, 0.13 mmol). The product is a yellow solid. Yield 192 mg, 86%. Anal. Found: C, 68.26; H, 4.74; N, 1.63. $C_{102}H_{84}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 69.34; H, 4.79; N, 1.58%. The sample was probably contaminated with solvents, for example $C_{102}H_{84}Cl_2N_2O_2P_4Ru_2 \cdot 0.5CH_2Cl_2$ Calc.: C, 68.05; H, 4.73; N, 1.55%. IR (KBr, cm^{-1}): 2099 vs [ν(C≡N)], 1950 vs [ν(C≡O)].

2.11. *[(μ-NC$_5$H$_4$–C$_5$H$_4$N)RuCl(CO)(PPh$_3$)$_2$(μ-CH=CH–C$_6$H$_4$–CH=CH)RuCl(CO)(PPh$_3$)$_2$]$_x$, **8a***

To a solution of **2a** (200 mg, 0.133 mmol) in 8 ml CH_2Cl_2 was added 4,4′-bipyridine (21 mg, 0.13 mmol). The reaction mixture turned to orange brown and was stirred under nitrogen for an hour at room temperature to give a brown orange solid. The solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried under vacuum. The solid is insoluble in common organic solvents. Yield 183 mg, 83%. Anal. Found: C, 67.66; H, 4.80; N, 1.38. $C_{94}H_{76}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 67.91; H, 4.60; N, 1.69%. IR (KBr, cm^{-1}): 1928 vs [ν(C≡O)].

2.12. *[(μ-NC$_5$H$_4$–C$_5$H$_4$N)RuCl(CO)(PPh$_3$)$_2$(μ-CH=CH–C$_6$H$_4$–C$_6$H$_4$CH=CH)RuCl(CO)(PPh$_3$)$_2$]$_x$, **8b***

The procedure is analogous to that for **8a**, starting from **2b** (200 mg, 0.126 mmol) and 4,4′-bipyridine

(20 mg, 0.126 mmol). The product is an orange brown solid. Yield 183 mg, 83%. Anal. Found: C, 68.15; H, 4.57; N, 1.73. $C_{100}H_{80}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 69.08; H, 4.64; N, 1.61%. The sample was probably contaminated with solvents, for example $C_{100}H_{80}Cl_2N_2O_2P_4Ru_2 \cdot 0.5CH_2Cl_2$ Calc.: C, 67.78; H, 4.58; N, 1.57%. IR (KBr, cm^{-1}): 1937 vs [ν(C≡O)].

2.13. *[RuCl(CO)(PCy_3)$_2$]$_2$(μ-CH=CH–C_6H_4–CH=CH), **10***

The experimental procedure was analogous to that described for **2a**; starting materials were $RuHCl(CO)(PCy_3)_2$ (200 mg, 0.276 mmol) and phenylacetylene (17.4 mg, 0.138 mmol). The product is a purple red solid. Yield 188 mg, 87%. Anal. Found: C, 64.07; H, 8.49. $C_{84}H_{140}Cl_2O_2P_4Ru_2$ Calc.: C, 63.89; H, 8.94%. IR (Nujol, cm^{-1}): 1907 vs [ν(C≡O)]. ^{1}H NMR ($CDCl_3$): δ 8.28 (d, J(HH) = 13.3 Hz, 2 H, Ru–CH), 6.82 (s, 4 H, C_6H_4), 5.82 (d, J(HH) = 13.3 Hz, 2 H, =CH), 2.59–1.13 (m, PCy_3). ^{31}P NMR ($CDCl_3$): δ 29.1 (s).

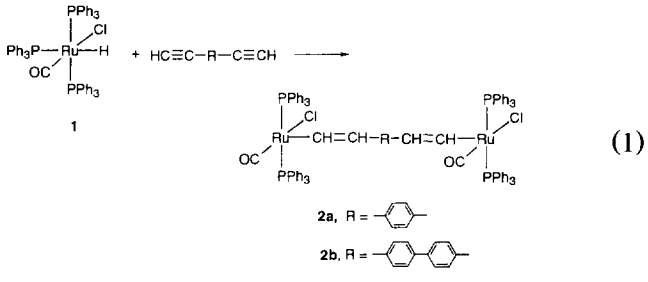
2.14. *[RuCl(CO)(C_8H_9N≡C)(PCy_3)$_2$]$_2$(μ-CH=CH–C_6H_4–CH=CH), **11***

To a solution of **10** (200 mg, 0.128 mmol) in 8 ml CH_2Cl_2 was added 2,6-dimethylphenyl isocyanide (37 mg, 0.28 mmol). The reaction mixture turned to orange brown and was stirred under nitrogen for 15 min at room temperature. After that, the volume of mixture was reduced to 1 ml under vacuum and 15 ml of ether was added to give a brown precipitate. The solid was collected by filtration, washed with ether (20 ml) and hexane (20 ml), and then dried under vacuum. Yield 176 mg, 76%. Anal. Found: C, 66.76; H, 8.33; N, 1.49. $C_{102}H_{158}Cl_2N_2O_2P_4Ru_2$ Calc.: C, 66.98; H, 8.65; N, 1.52%. IR (Nujol, cm^{-1}): 2105 vs [ν(C≡N)], 1922 vs [ν(C≡O)]. ^{1}H NMR ($CDCl_3$): δ 8.35 (d, J(HH) = 13.3 Hz, 2 H, Ru–CH=), 7.36–7.10 (m, 10 H, C_6H_4, 2 C_6H_3), 6.63 (d, J(HH) = 13.3 Hz, 2 H, =CH), 2.65–1.15 (m, PCy_3, CH_3). ^{31}P NMR ($CDCl_3$): δ 28.1 (s).

3. Results and discussion

3.1. Synthesis of conjugated dimeric complexes by insertion reactions of $RuHCl(CO)(PPh_3)_3$

It has been reported that monomeric five-coordinate ruthenium vinyl complexes $RuCl(CH=CH–R)(CO)(PPh_3)_2$ can be prepared from insertion reactions of RC≡CH with $RuHCl(CO)(PPh_3)_3$ [21]. In principle, reactions of HC≡C–R–C≡CH with $RuHCl(CO)(PPh_3)_3$ can lead to coordinatively unsaturated dimeric complexes $[RuCl(CO)(PPh_3)_2]_2$(μ-CH=CH–R–CH=CH), which can be linked with appropriate bifunctional ligands to give polymers. Thus we studied the reactions of HC≡C–Ar–C≡CH (Ar = C_6H_4, C_6H_4–C_6H_4) with $RuHCl(CO)(PPh_3)_3$. Reactions of $RuHCl(CO)(PPh_3)_3$ with *p*-diethynyl benzene and 4,4′-bis(ethynyl) biphenyl produced the red dimeric complexes $[RuCl(CO)(PPh_3)_2]_2$(μ-CH=CH–Ar–CH=CH), **2**, in high yields (Eq. (1)). During the course of this work, the synthesis of **2a** was briefly reported [13]. It is interesting to note that monomeric vinyl complexes such as $RuCl(CH=CH–R)(CO)(PPh_3)_2$ [21] and $RuCl(CH=CH–R)(CO)(P(i\text{-}Pr)_3)_2$ [22] are also red in color.

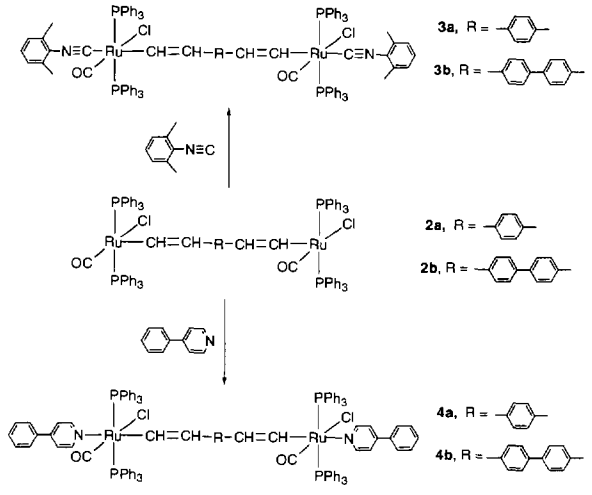


(1)

The red complexes **2** are soluble in CH_2Cl_2, $CHCl_3$ and benzene, and insoluble in ether, methanol and hexane. The complexes have been characterized by elemental analysis, ^{1}H and ^{31}P NMR and IR spectroscopy. The ^{31}P NMR spectra of complexes **2** in $CDCl_3$ displayed singlets at 29.0 ppm for **2a** and 29.8 ppm for **2b**, indicating that the two phosphine ligands are equivalent and *trans* to each other. Complexes **2** showed a strong IR band near 1930 cm^{-1} assignable to ν(CO). The ^{1}H NMR spectra showed resonances for the two vinylic hydrogen atoms near 8.3 and 5.5 ppm with J(HH) = 13–14 Hz. The magnitude of the coupling constants indicates that the two vinylic protons are *trans* to each other and that the acetylenes are *cis* inserted into the Ru–H bond [21–27]. The geometry of the dimeric complexes around ruthenium was assigned by analogy to those of the monomeric complexes $RuCl(CR=CHR')(CO)(PR''_3)_2$, some of which have been characterized by X-ray diffraction [21,22].

3.2. Formation of six-coordinate dimeric complexes

As complexes **2** are coordinatively unsaturated, one might expect that coordination oligomers or polymers would be produced if one uses appropriate bifunctional ligands to link the metal centers. Since coordination polymers with metal centers bridged by diisocyanoaryls [3] or bipyridine derivatives [28] have been extensively studied and some of these polymers are reported to exhibit electrical conducting properties, it would be interesting to link dimers **2** with these ligands to prepare



Scheme 1.

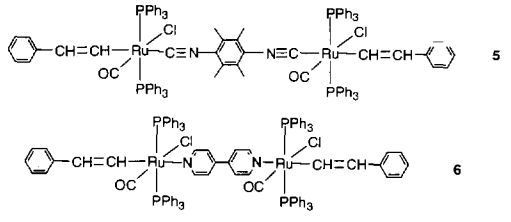
polymers. To determine if complexes **2** can be used as precursors to such polymers, and to prepare model compounds for the targeting polymers, we have studied the reactivity of **2** and $RuCl(CH{=}CHPh)(CO)(PPh_3)_2$ toward 2,6-dimethylphenyl isocyanide, 4-phenylpyridine, 2,3,5,6-tetramethylphenyl diisocyanide and 4,4′-bipyridine.

Treatment of **2** with 2,6-dimethylphenyl isocyanide and 4-phenylpyridine in CH_2Cl_2 resulted in an almost instantaneous color change of the reaction mixture, from which, after concentration and addition of ether, complexes **3** and **4** were isolated in high yields (see Scheme 1).

The geometry of the adducts **3** and **4** around ruthenium was assigned by analogy to those of similar reported six-coordinate monomeric complexes. Complexes $RuCl(CH{=}CHR)(CO)(PPh_3)_2$ are known to react with L, such as Me_2Hpz (3,5-dimethylpyrazole) [29], BSD (2,1,3-benzoselenadiazole) [26] and RNC [30], to give the six-coordinate compounds $RuCl(CH{=}CHR)(CO)(PPh_3)_2(L)$ with two mutually *trans* PPh_3 ligands and the vinyl group *cis* to the carbonyl ligand.

Consistent with the structure, the ^{31}P NMR spectra showed the triphenylphosphine signal as a singlet near 25 ppm, indicating that the two PPh_3 are *trans* disposed. The IR spectra of the adducts of 2,6-dimethylphenyl isocyanide **3** showed a strong absorption band in the region 2099–2116 cm^{-1} assignable to $\nu(C{\equiv}N)$, and a strong band near 1960 cm^{-1} assignable to $\nu(CO)$. The IR spectra of adducts **4** displayed a strong band near 1930 cm^{-1} assignable to $\nu(CO)$. The structures of complexes **4a** and **4b** are also supported by the ^{13}C NMR data. Unfortunately, the solubility of complexes **3a** and **3b** is too low to obtain ^{13}C NMR spectra.

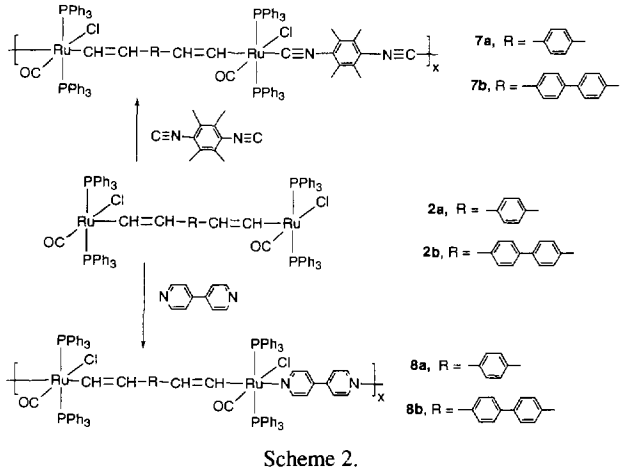
Dinuclear complexes **5** and **6**, in which the two metal centers are bridged with 2,3,5,6-tetramethylphenyl diisocyanide and 4,4′-bipyridine, could also be easily prepared by reactions of $RuCl(CO)(CH{=}CHPh)(PPh_3)_2$ with 2,3,5,6-tetramethylphenyl diisocyanide and 4,4′-bipyridine respectively. The IR and ^{31}P spectroscopic data for complexes **5** and **6** are very similar to those of **3** and **4**.



3.3. Synthesis of conjugated ruthenium organometallic oligomers or polymers with metal–vinyl linkages

Easy production of adducts of isocyanides and pyridine derivatives from complexes **2** and $RuCl(CH{=}CHPh)(PPh_3)_2$ in high yields infers that complexes **2** can be used to prepare oligomeric or polymeric complexes.

Treatment of red solutions of **2** with 2,3,5,6-tetramethylphenyl diisocyanide or 4,4′-bipyridine in CH_2Cl_2 resulted in an almost instantaneous precipitation of yellow or greenish yellow solids of the oligomeric or polymeric complexes **7** and **8** (see Scheme 2). Unfortunately, these solids are too insoluble in common organic solvents to collect NMR and GPC data. Thus they were primarily characterized by elemental analysis and IR spectroscopy. In particular, the IR spectra of the insoluble materials are quite similar to those of analogous dimers. For example, the stretching frequencies of the C≡O and C≡N groups of dimer **3a** appeared at 1960 and 2099 cm^{-1}, and those of **7a** at 1950 and 2090 cm^{-1}; the stretching frequency of the C≡O group of dimer **4b** was observed at 1928 cm^{-1} and that for polymer **8b** appeared at 1937 cm^{-1}.



Scheme 2.

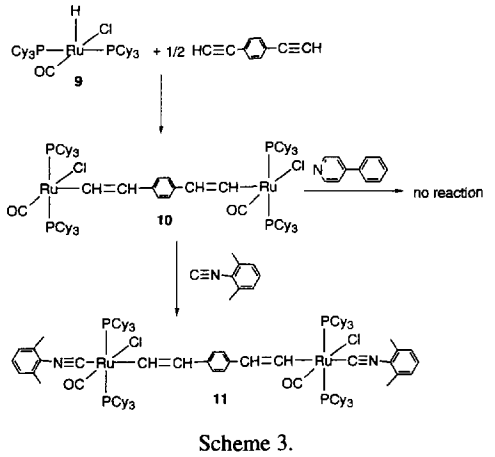
3.4. Synthesis of conjugated dimeric complexes by insertion reactions of $RuHCl(CO)(PCy_3)_2$

Soluble rigid-rod organometallic polymers have been achieved with alkylated phosphines such as $P(n\text{-}Bu)_3$. To explore the possibility of preparing soluble polymers analogous to **7** or **8**, we have studied the model reactions starting from $RuHCl(CO)(PCy_3)_2$ (**9**) (see Scheme 3).

As expected, complex **9** reacted smoothly with *p*-diethynyl benzene to give the red dimeric complexes $[RuCl(CO)(PCy_3)_2]_2(\mu\text{-}CH{=}CH{-}C_6H_4{-}CH{=}CH)$ (**10**). Complex **10** is readily characterized by the ^1H NMR which showed vinyl signals at 8.28 (Ru–CH) and 5.82 ppm (=CH) and the ^{31}P NMR which showed the PCy_3 signals at 29.1 ppm.

In order to determine if the dimeric complex **10** can be linked with bipyridine derivatives or diisocyanides to give polymers, complex **10** was treated with 4-phenylpyridine and 2,6-dimethylphenyl isocyanide. No reaction was observed between 4-phenylpyridine and complex **10**, presumably due to the steric bulkiness of the PCy_3 ligand. On the other hand, complex **10** reacted with 2,6-dimethylphenyl isocyanide to give complex **11**.

Complex **11** is characterized by ^1H, ^{31}P NMR and IR spectroscopy. The ^{31}P NMR spectra showed the PCy_3 signal as a singlet at 28.1 ppm, indicating that the two PCy_3 are *trans* disposed. The IR spectrum showed strong absorption bands at 2105 cm^{-1} assignable to $\nu(C{\equiv}N)$ and at 1922 cm^{-1} assignable to $\nu(CO)$. The ^1H NMR spectrum (in $CDCl_3$) showed vinyl signal at 8.35 (Ru–CH) and 6.63 ppm (=CH). Like complexes **3**, the solubility of complex **11** is so low that good ^{13}C NMR spectrum could not be obtained. Thus it was reasoned that incorporation of PCy_3 may not improve the solubility of the targeting polymers and therefore no further study was carried out. Use of phosphines with long alkyl chains such as $P(n\text{-}Bu)_3$ may produce polymers soluble in organic solvents. Unfortunately, there are no suitable starting materials for the preparation based on the chemistry described above.



Scheme 3.

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References

[1] N.J. Long, Angew. Chem., Int. Ed. Engl. 34 (1995) 21 and references cited therein; S. Lotz, P.H. Van Rooyen, R. Mayer, Adv. Organomet. Chem. 37 (1995) 219; H. Lang, Angew. Chem., Int. Ed. Engl. 33 (1994) 547; W. Beck, B. Niemer, M. Wieser, Angew. Chem., Int. Ed. Engl. 32 (1993) 923.

[2] M.J. Irin, G. Jia, N.C. Payne, R.J. Puddephatt, Organometallics 15 (1996) 51 and references cited therein; C.W. Faulkner, S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 482 (1994) 139; M.S. Khan, A.K. Kakkar, S.L. Inghan, P.R. Raithby, J. Lewis, B. Spencer, F. Wittmann, R.H. Friend, J. Organomet. Chem. 472 (1994) 247; R.R. Tykwinski, P.J. Stang, Organometallics 13 (1994) 3203; G. Jia, R.J. Puddephatt, J.D. Scott, J.J. Vittal, Organometallics 12 (1993) 3565; Z. Atherton, C.W. Faulkner, S.L. Ingham, A.K. Kakkar, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 462 (1993) 265; G. Frapper, M. Kertesz, Inorg. Chem. 32 (1993) 732; M.S. Khan, S.J. Davies, A.K. Kakkar, D. Schwartz, B. Lin, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 424 (1992) 87; J. Lewis, M.S. Khan, A.K. Kakkar, B.F.G. Johnson, T.B. Marder, H.B. Fyfe, F. Wittman, R.H. Friend, A.E. Dray, J. Organomet. Chem. 425 (1992) 165; H.B. Fyfe, M. Mlekuz, D. Zargarian, N.J. Taylor, T.B. Marder, J. Chem. Soc., Chem. Commun. (1991) 187.

[3] A.M. Bradford, E. Kristof, M. Rashidi, D.S. Yang, N.C. Payne, R.J. Puddephatt, Inorg. Chem. 33 (1994) 2355; M. Rashidi, E. Kristof, J.J. Vittal, R.J. Puddephatt, Inorg. Chem. 33 (1994) 1497; M. Hanack, in P. Wisian-Neilson, H.R. Allock, K.J. Wynne (Eds.), Inorganic and Organometallic Polymers II. Advanced Materials and Intermediates, ACS, Washington, DC, 1994, p. 472 and references cited therein; G. Jia, N.C. Payne, J.J. Vittal, R.J. Puddephatt, Organometallics 12 (1993) 4772; M. Hanack, H. Ryu, Synth. Met. 46 (1992) 13 and references cited therein; I. Feinstein-Jaffe, C. Barash, Inorg. Chim. Acta 185 (1991) 3 and references cited therein; I. Feinstein-Jaffe, F. Frowlow, L. Wackerle, A. Goldman, A. Efraty, J. Chem. Soc., Dalton. Trans. (1988) 469; I. Feinstein-Jaffe, I. Brain, D. Mahalu, S. Cohen, S.A. Lawrence, Inorg. Chim. Acta 154 (1988) 129; U. Keppler, M. Hanack, Chem. Ber. 119 (1986) 3363; S. Deger, M. Hanack, Synth. Met. 13 (1986) 319; U. Keppler, M. Hanack, O. Schneider, W. Stoffler, Tetrahedron Lett. 25 (1984) 3679; O. Lavastre, M. Even, P.H. Dixneuf, A. Pacreau, J.P. Vairon, Organometallics 15 (1996) 1530.

[4] W. Siebert, in R.M. Laine (Ed.), Inorganic and Organometallic Polymers with Special Properties, Kluwer, Dordrecht, 1992, p. 207 and references cited therein.

[5] B.F. Bush, J.J. Lagowski, Organometallics 7 (1988) 1945 and references cited therein; R. Arnold, S.A. Matchett, M. Rosenblum, Organometallics 7 (1988) 2261 and references cited therein.

[6] J.L. Bredas, R.R. Chance (Eds.), Conjugated Polymeric Materials: Opportunity in Electronics, Optoelectronics, and Molecular Electronics, Kluwer Academic, Dordrecht, 1990; T.A. Skotheim (Ed.), Electroresponsive Molecular and Polymeric Systems, Marcel Dekker, New York, 1991; T.A. Skotheim (Ed.), Handbook of Conducting Polymers, Marcel Dekker, New York, 1986.

[7] R. McDonald, K.C. Sturge, A.D. Hunter, L. Shilliday, Organometallics 11 (1992) 893; K.C. Sturge, A.D. Hunter, R. McDonald, B.D. Sanstarsiero, Organometallics 11 (1992) 3056.
[8] N. Rajapakse, B.R. James, D. Dolphin, Can. J. Chem. 68 (1990) 2274.
[9] R.M. Bullock, F.R. Lemke, D.J. Szalda, J. Am. Chem. Soc. 112 (1990) 3244; F.R. Lemke, D.J. Szalda, R.M. Bullock, J. Am. Chem. Soc. 113 (1991) 8466.
[10] M.B. Sponsler, Organometallics 14 (1995) 1920 and references cited therein; B.A. Etzenhouser, Q. Chen, M.B. Sponsler, Organometallics 13 (1994) 4176 and references cited therein.
[11] H.H. Fox, J.K. Lee, L.Y. Park, R.R. Schrock, Organometallics 12 (1993) 759.
[12] L.K. Myers, D.M. Ho, M.E. Thompson, C. Langhoff, Polyhedron 14 (1995) 57.
[13] A. Santos, J. López, J. Montoya, P. Noheda, A. Romero, A.M. Echararren, Organometallics 13 (1994) 3605.
[14] J. Breimair, M. Steimann, W. Wagner, W. Beck, Chem. Ber. 123 (1990) 7.
[15] C.M. Mitchel, F.G.A. Stone, J. Chem. Soc., Chem. Commun. (1970) 1264; J. Chem. Soc., Dalton Trans. (1972) 102; J.A.J. Jarvis, A. Johnson, R.J. Puddephatt, J. Chem. Soc., Chem. Commun. (1973) 373; J. Chem. Soc., Dalton Trans. (1978) 980.
[16] G. Erker, W. Frömberg, K. Angermund, R. Schlund, C. Krüger, J. Chem. Soc., Chem. Commun. (1986) 372; K.D. Grande, A.J. Kunin, L.S. Stuhl, B.M. Foxman, Inorg. Chem. 22 (1983) 1791; E.O. Fisher, D. Wittmann, D. Himmelreich, D. Neugebauer, Angew. Chem., Int. Ed. Engl. 21 (1982) 444.
[17] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 48.
[18] F.G. Moers, J.P. Langhout, Rec. Trav. Chim. 91 (1972) 591.
[19] S. Takahashi, N. Hagihara, Y. Kurayama, K. Sonogashira, Synthesis (1980) 627; D.E. Ames, D. Bull, C. Takundwa, Synthesis (1981) 364.
[20] G.W. Gokel, R.P. Widera, W.P. Weber, F.A. South-Bachiller, S. Masamune, C.J. Talkowski, W.A. Sheppard, Org. Synth. 55 (1975) 96.
[21] M.R. Torres, A. Vegas, A. Santos, J. Ros, J. Organomet. Chem. 309 (1986) 169.
[22] M.A. Esteruelas, L.A. Oro, C. Valero, Organometallics 14 (1995) 3596; M.A. Esteruelas, J. Herrero, L.A. Oro, Organometallics 12 (1993) 2377; H. Werner, M.A. Esteruelas, H. Otto, Organometallics 5 (1986) 2295; M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, B. Zeier, Organometallics 13 (1994) 4258; H. Werner, U. Meyer, K. Peters, H.G. von Schnering, Chem. Ber. 122 (1989) 1097.
[23] A. Santos, J. López, L. Matas, J. Ros, A. Galán, A.M. Echavarren, Organometallics 12 (1993) 4215; Y. Wakatsuki, H. Yamazaki, Y. Maruyama, I. Shimizu, J. Organomet. Chem. 430 (1992) C60; R.M. Torres, A. Santos, J. Ros, X. Solans, Organometallics 6 (1987) 1091; M.R. Torres, A. Vegas, A. Santos, J. Ros, J. Organomet. Chem. 326 (1987) 413; J. Cartwright, A.F. Hill, J. Organomet. Chem. 429 (1992) 229; A.M. Castano, A.M. Echavarren, J. López, A. Santos, J. Organomet. Chem. 379 (1989) 171; A.F. Hill, R.P. Melling, J. Organomet. Chem. 396 (1990) C22.
[24] J.D. Vessey, R.J. Mawby, J. Chem. Soc., Dalton Trans. (1993) 51; J.D. Bray, R.J. Mawby, J. Chem. Soc., Dalton Trans. (1989) 589.
[25] A. Remoro, A. Santos, J. López, A.M. Echavarren, J. Organomet. Chem. 391 (1990) 219; A. Remoro, A. Santos, A. Vagas, Organometallics 7 (1988) 1988 and references cited therein.
[26] M.C.J. Harris, A.F. Hill, Organometallics 10 (1991) 3903; J. Organomet. Chem. 438 (1992) 209.
[27] J. López, A. Romero, A. Santos, A. Vagas, A.M. Echavarren, P. Noheda, J. Organomet. Chem. 373 (1989) 249; A.M. Echavarren, J. Lopez, A. Santos, A. Romero, J.A. Hermoso, A. Vagas, Organometallics 10 (1991) 2371.
[28] M. Hanack, A. Datz, R. Fay, K. Fischer, U. Keppler, J. Koch, J. Metz, M. Mezger, O. Schneider, H.J. Schulze, in T.A. Skotheim (Ed.), Handbook of Conducting Polymers, vol. 1, Marcel Dekker, New York, 1986, p. 133 and references cited therein.
[29] M.R. Torres, A. Santos, A. Perales, J. Ros, J. Organomet. Chem. 353 (1988) 221.
[30] J. Montoya, A. Santos, J. López, A.M. Echavarren, J. Ros, A. Romero, J. Organomet. Chem. 426 (1992) 383.