Organometallics **1996,** *15,* 3634−3636

Dimeric Ruthenium Complexes with C_5H_2 and C_5H Bridges

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Received June 21, 1996⊗

Summary: Treatment of $[Cp^*Ru(dppe)]BF_4$ *with 0.5 equiv of* $HC{\equiv}CCH(OH)C{\equiv}CH$ *in THF led to the formation of the* C_5H_2*-bridged compound* $[Cp^*(dppe)Ru{=}C{=}C{=}CHCH{=}C{=}Ru(dppe)Cp^*](BF_4)_2$*. The* C_5H_2*-bridged compound reacted with alumina to give the* C_5H*-bridged compound* $[Cp^*(dppe)Ru{=}C{=}C{=}CHC{\equiv}CRu(dppe)Cp.^*]BF_4$*. These reactions were extended to prepare the analogous complex* $[Cp(PPh_3)_2Ru{=}C{=}CHC{\equiv}CRu(PPh_3)_2Cp]BF_4$*.*

Dimeric organometallic compounds with π-conjugated bridges have recently attracted considerable attention, because of their unusual intrinsic chemical, physical, and material properties.[1,2] Some of the most interesting conjugated organometallic dimeric complexes reported recently include those with C_x-bridged complexes $L_nM\text{-}C_xM'L_{n'}$ (e.g. $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_5)Mn(CO)_2(C_5Cl_5)]^+$),[3] $(CH)_x$-bridged complexes (e.g. $[Cp(dppm)FeCH{=}CHCH{=}CHFe(dppm)Cp]$),[4] and C_4R_2-bridged complexes with $M{\equiv}C$ linkages such as $[(Me_3SiNCH_2CH_2)_3N]Mo{\equiv}CCH{=}CHC{\equiv}Mo[N(CH_2CH_2NSiMe_3)_3]$[5] or complexes with $M{=}C$ linkages such as $[(C_5H_4SiMe_3)_2(CO)Nb{=}C{=}CMeCMe{=}C{=}Nb(CO)(C_5H_4SiMe_3)_2](BPh_4)_2$).[6] We are interested in the synthesis and properties of new types of conjugated organometallic dimeric and polymeric compounds. We now report the synthesis and characterization of the first isolable dimeric complexes with C_5H_2 and C_5H bridges.

Treatment of $[Cp^*Ru(dppe)]BF_4$ (generated in situ from the reaction of $Cp^*RuCl(dppe)$[7] with $AgBF_4$) with 0.5 equiv of $HC{\equiv}CCH(OH)C{\equiv}CH$[8] in THF led to a purple solution. A purple solid could be isolated in 82% yield from the reaction mixture. The elemental analysis and spectroscopic data confirm that the isolated product is the C_5H_2-bridged compound $[Cp^*(dppe)Ru{=}C{=}C{=}CHCH{=}C{=}Ru(dppe)Cp^*](BF_4)_2$ (**1**;[9] see Scheme 1). The $Ru_2(\mu\text{-}C_5H_2)$ assembly of complex **1** is indicated by ^{13}C NMR, which shows resonances at δ 353.7 (t, $J(PC) = 15.6$ Hz), 281.1 (t, $J(PC) = 19.6$ Hz), 188.9 (s), 132.8 (s), and 128.1(s) ppm for the five carbons in $Ru{=}C{=}C{=}CHCH{=}C{=}Ru$. The signals at 281.1, 188.9, and 132.8 ppm can be assigned to the $Ru{=}C{=}C{=}CH$ group,[10] and those at 353.7 and 128.1 ppm can be assigned to the $Ru{=}C{=}CH$ group.[10] The structure of **1** is further supported by ^1H NMR (in $CDCl_3$), which displays two signals at 3.90 (d, $J(HH) = 11.7$ Hz) and 6.01 (d, $J(HH) = 11.7$ Hz) ppm for the two $C{=}CH$ protons and two Cp^* signals at 1.63 and 1.49 ppm. Consistent with the structure, the ^{31}P NMR spectrum in $CDCl_3$ gives two singlets for the dppe ligand at 76.9 and 67.5 ppm. IR bands assignable to $\nu(C{=}C{=}CHCH{=}C)$ at ca. 1953 (s) and 1881 (m) cm^{-1} were also observed. The C_5H_2-bridged complex **1** has an intense purple color with strong absorption bands at 230 nm ($\epsilon = 7.8 \times 10^4\ M^{-1}\ cm^{-1}$) and 528 nm ($\epsilon = 4.2 \times 10^4\ M^{-1}\ cm^{-1}$). The band around 528 nm could be assigned to the intervalence charge-transfer absorption involving the $Ru(\mu\text{-}C_5H_2)Ru$ unit.

Compound **1** is likely formed via the dehydration of the intermediate $[Cp^*(dppe)Ru{=}C{=}CHCH(OH)CH{=}C{=}Ru(dppe)Cp^*](BF_4)_2$. Although we have not been able to isolate the intermediates yet, it has been established that reactions of metal complexes with simple 1-alkyn-

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⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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(2) (a) Lotz, S.; Van Rooyen, P. H.; Mayer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219. (b) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. (c) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923.

(3) See for example: (a) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199 and references therein. (b) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655 and references therein. (c) Zhou, Y.; Seyler, J. W.; Weng, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509. (d) Seyler, J. W.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802. (e) Weng, W.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3824. (f) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (g) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T. *J. Organomet. Chem.* **1993**, *450*, 209. (h) Caulton, K. G.; Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B.; Xue, Z. *Organometallics* **1992**, *11*, 321. (i) Crescenzi, R.; Sterzo, C. L. *Organometallics* **1992**, *11*, 4301. (j) Koutsantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2316.

(4) (a) Sponsler, M. B. *Organometallics* **1995**, *14*, 1920 and references therein. (b) Etzenhouser, B. A.; Chen, Q.; Sponsler, M. B. *Organometallics* **1994**, *13*, 4176. (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466 and references therein. (d) Bullock, R. M.; Lemke, F. R.; Szalda, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 3244.

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(6) (a) Antinolo, A.; Otero, A.; Fajardo, M.; Garcia-Yebra, C.; Gil-Sanz, R.; Lopez-Mardomingo, C.; Martin, A.; Gomez-Sal, P. *Organometallics* **1994**, *13*, 4679. (b) Werner, W.; Rappert, T.; Nurnberg, O. *Organometallics* **1993**, *12*, 1359. (c) Beddoes, R. L.; Bitcon, C.; Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *367*, C21. (d) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910.

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(8) Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 3483.

(9) Selected data for **1** are as follows. Anal. Calcd for $C_{77}H_{80}P_4B_2F_8Ru_2$: C, 61.45; H, 5.36. Found: C, 61.39; H, 5.50. IR (KBr, cm^{-1}): 3055 (w), 2909 (w), 1953 (s), 1881 (m), 1627 (w), 1529 (s), 1438 (s), 1168 (m), 1061 (s). UV/vis (CH_2Cl_2): λ_{max} (ϵ) 528 ($4.2 \times 10^4\ M^{-1}\ cm^{-1}$), 230 nm ($7.8 \times 10^4\ M^{-1}\ cm^{-1}$). ^1H NMR ($CDCl_3$): δ 7.03−7.80 (m, 40H, 8Ph), 6.01 (d, $^3J(HH) = 11.7$ Hz, 1H, $Ru{=}C{=}C{=}CH$), 3.90 (d, $^3J(HH) = 11.7$ Hz, 1H, $Ru{=}C{=}CH$), 2.40−2.70 (m, 8H, $4CH_2$), 1.63 (s, 15H, $5CH_3$), 1.49 (s, 15H, $5CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 76.9 (s), 67.5 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 353.7 (t, $J(PC) = 15.6$ Hz, $Ru{=}\mathit{C}{=}CH$), 281.1 (t, $J(PC) = 19.6$ Hz, $Ru{=}\mathit{C}{=}C{=}CH$), 188.9 (s, $Ru{=}C{=}\mathit{C}{=}CH$), 132.8 (s, $Ru{=}C{=}C{=}\mathit{C}H$), 128.1 (s, $Ru{=}C{=}\mathit{C}H$), 135.3−128.9 (m, $2PPh_2$), 106.0 (s, C_5Me_5), 101.7 (s, C_5Me_5), 30.2−28.7 (m, CH_2), 10.7 (s, $C_5\mathit{Me}_5$), 10.5 (s, $C_5\mathit{Me}_5$).

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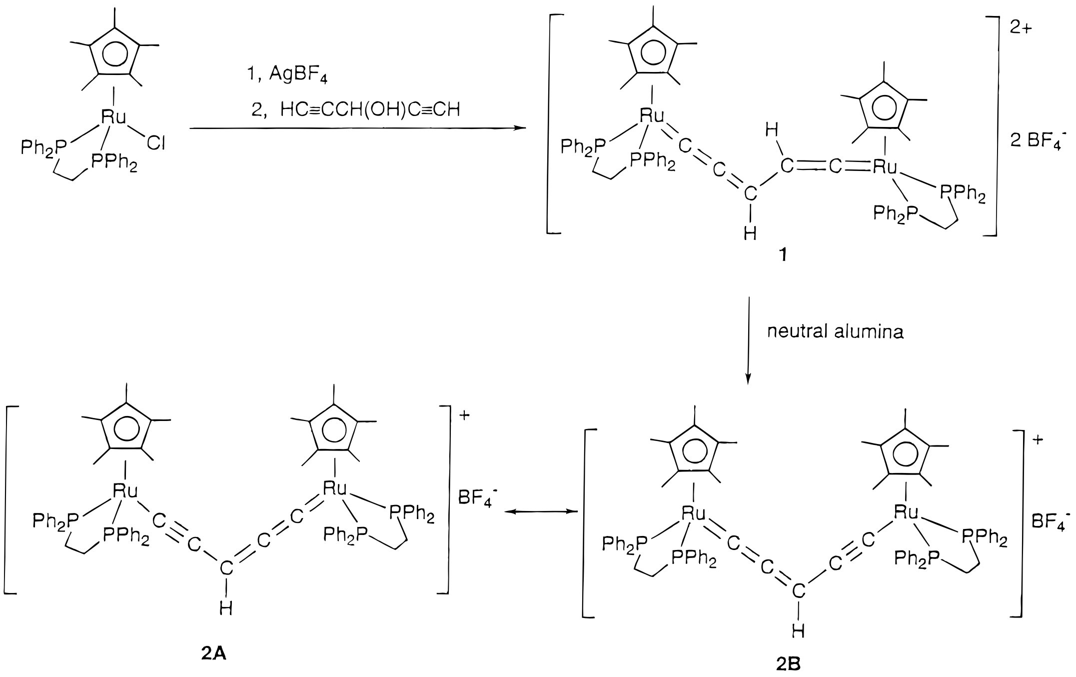
S0276-7333(96)00501-8 CCC: $12.00

Scheme 1



3-ols could lead to allenylidenes.[10,11] For example, reactions of 1-alkyn-3-ols with ruthenium complexes such as (η^5-C_5R_5)RuCl(PR'_3)$_2$ in polar media lead to hydroxyvinylidene intermediates which spontaneously dehydrate to form either allenylidene or vinylvinylidene complexes.[11]

Compound **1** is very reactive, and it was converted readily to a new compound upon contact with alumina or silica gel. Thus, addition of neutral alumina to a purple CH_2Cl_2 solution containing **1** caused an immediate color change from purple to deep blue, from which a stable blue microcrystalline solid was isolated in 88% yield based on **1**. The isolated product is soluble in acetone, chloroform, dichloromethane, and tetrahydrofuran but insoluble in benzene and hexane. The elemental analysis and spectroscopic data confirm that the isolated product is the C_5H-bridged compound [Cp*(dppe)Ru=C=C=CHC≡CRu(dppe)Cp*]BF_4 (**2**).[12] Thus, deprotonation of complex **1** by alumina occurred during the reaction. Deprotonation of vinylidene complexes with alumina to give the corresponding σ-acetylide complexes have been noted previously.[13] As evidenced by its NMR spectra, complex **2** has a delocalized structure with two identical ruthenium centers. The structures **2A** and **2B** are two of the possible resonance structures for complex **2**. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α, C_β, and C_γ resonances were observed at δ 225.6 (t, $^2J(PC) = 20.9$ Hz), 163.1 (s), and 128.4 (s) ppm, respectively. Consistent with the structure, the ^{31}P NMR spectrum in $CDCl_3$ displays a singlet at δ 78.4 ppm for the dppe ligand and the ^1H NMR spectrum in $CDCl_3$ exhibits a singlet at δ 1.51 ppm for the two Cp* rings. A strong IR band assignable to ν(C=C=C) at ca. 1881 cm^{-1} was also observed.

To test if the above reactions are general, the reactions of [CpRu(PPh_3)$_2$]BF_4 (generated in situ from the reaction of CpRuCl(PPh_3)$_2$[14] with $AgBF_4$) with HC≡CCH(OH)C≡CH were carried out. Treatment of [CpRu(PPh_3)$_2$]BF_4 with 0.5 equiv of HC≡CCH(OH)C≡CH in THF also led to a purple solution. When the purple solution was passed through a short column with neutral alumina as the solid phase, the analogous C_5H-bridged compound [Cp(PPh_3)$_2$Ru=C=C=CHC≡CRu(PPh_3)$_2$Cp]BF_4 (**3**)[15] was obtained in 66% yield based on CpRuCl(PPh_3)$_2$.

Both the C_5H-bridged complexes **2** and **3** have an intense blue color with strong absorption bands at 230 ($\epsilon = 8.0 \times 10^4$ M^{-1} cm^{-1}) and 630 nm ($\epsilon = 5.8 \times 10^4$ M^{-1} cm^{-1}) for **2** and at 230 ($\epsilon = 6.8 \times 10^4$ M^{-1} cm^{-1}) and 600 nm ($\epsilon = 7.2 \times 10^4$ M^{-1} cm^{-1}) for **3**. The bands around 600 nm can be assigned to intervalence charge transfer absorptions involving Ru=C=C=CHC≡CRu. The molar extinction coefficients for the intervalence charge transfer absorptions are much higher than those

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[11] See for example: (a) Touchard, D.; Pirio, N.; Dixneuf, P. H. *Organometallics* **1995**, *14*, 4920. (b) Le Ladadec, R.; Roman, E.; Toupet, L.; Muller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030 and references therein. (c) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1 and references therein. (d) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972–1980.

[12] Selected data for **2** are as follows. Anal. Calcd for $C_{77}H_{79}P_4BF_4Ru_2$: C, 65.25; H, 5.62. Found: C, 65.16; H, 5.60. IR (KBr, cm^{-1}): 3056 (w), 2903 (w), 1881 (s), 1575 (w), 1437 (m), 1096 (m), 1029 (m), 698 (m), 533 (m). UV/vis (CH_2Cl_2): λ_{max} (ϵ) 630 (5.8×10^4 M^{-1} cm^{-1}), 230 nm (8.0×10^4 M^{-1} cm^{-1}). ^1H NMR ($CDCl_3$): δ 7.05–7.48 (m, 40H, 8Ph), 2.30–2.74 (m, 8H, 4CH_2), 1.51 (s, 30H, 10CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.4 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 225.6 (t, $J(PC) = 20.9$ Hz, C(α), 163.1 (s, Cβ), 128.4 (s, Cγ), 135.8–134.5 (m, *ipso* Ph), 133.0–132.5 (m, *m*-Ph), 130.2 (s, *p*-Ph), 129.9 (s, *p*-Ph), 128.5 (s, Cγ), 128.2–127.6 (m, *o*-Ph), 97.5 (s, C_5Me_5), 29.8–29.2 (m, CH_2), 9.7 (s, C_5Me_5).

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[14] Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R.; Ittel, S. D. *Inorg. Synth.* **1990**, *28*, 270.

[15] Selected data for **3** are as follows. Anal. Calcd for $C_{87}H_{71}P_4BF_4Ru_2$: C, 68.33; H, 4.68. Found: C, 68.19; H, 5.06. IR (KBr, cm^{-1}): 3052 (w), 1881 (s), 1572 (w), 1481 (m), 1435 (m), 1091 (m). UV/vis (CH_2Cl_2): λ_{max} (ϵ) 230 (6.8×10^4 M^{-1} cm^{-1}), 600 nm (7.2×10^4 M^{-1} cm^{-1}). ^1H NMR (CD_2Cl_2): δ 7.88 (quintet, $^5J(PH) = 1.08$ Hz, 1H, –CH=), 7.33–7.13 (m, 60H, 12Ph), 4.72 (s, 10H, 2Cp). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.8 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 228.5 (t, $^2J(PC) = 21.7$ Hz, Cα), 168.5 (s, Cβ), 133.1 (s, Cγ), 135.7–136.9 (m, *ipso*-C, Ph), 133.3, 127.8 (each m, *o,p*-Ph), 129.5 (s, *p*-Ph).

observed for Creutz−Taube ions[16] and are of magnitude similar to those observed for $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_3)Mn(CO)_2Cp)]^+$ (ϵ_{max}(392 nm) = 56 000 M^{-1} cm^{-1}) and $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_5)Mn(CO)_2(C_5Cl_5)]^+$ (ϵ_{max}(480 nm) = 60 000 M^{-1} cm^{-1}).[3a,e]

In summary, we have developed surprisingly easy methods to prepare dimeric complexes with C_5H_2 and C_5H bridges. We are in the process of investigating the properties of complexes **1**−**3** and extending the chemistry to synthesize other conjugated C_xH_y-bridged complexes.

Acknowledgment. We acknowledge financial support from the Hong Kong Research Grants Council and the Hong Kong University of Science and Technology.

OM960501M

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