Organometallics **2003,** *22,* 737−743

Synthesis and Characterization of Bimetallic Ruthenium Complexes with $(CH)_6$ and Related Bridges

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Received September 16, 2002

Treatment of $RuHCl(CO)(PPh_3)_3$ with (*E*)-HC≡CCH=CHC≡CH produces $[RuCl(CO)(PPh_3)_2]_2(\mu$-(*E*,*E*,*E*)-CH=CHCH=CHCH=CH). The latter complex reacts with PMe_3, 4-phenylpyridine (PhPy), and 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP) to give $[RuCl(CO)(PMe_3)_3]_2(\mu$-CH=CHCH=CHCH=CH), $[RuCl(CO)(PhPy)(PPh_3)_2]_2(\mu$-CH=CHCH=CHCH=CH), and $[RuCl(CO)(PMP)]_2(\mu$-CH=CHCH=CHCH=CH), respectively. Treatment of $[RuCl(CO)(PPh_3)_2]_2(\mu$-(*E*,*E*,*E*)-CH=CHCH=CHCH=CH) with *t*-BuNC and $NaBPh_4$ gives $\{[Ru(t\text{-}BuNC)_3(PPh_3)_2]_2(\mu$-COCH=CHCH=CHCH=CHCO)$\}(BPh_4)_2$, the structure of which has been confirmed by X-ray diffraction. Treatment of $RuHCl(CO)(PPh_3)_3$ with excess (*Z*)-HC≡CCH=CHC≡CH followed by PMe_3 produces RuCl((*E*,*Z*)-CH=CHCH=CHC≡CH)(CO)$(PMe_3)_3$. The mononuclear complex reacts with $RuHCl(CO)(PPh_3)_3$ to give $(PMe_3)_3(CO)ClRu$−CH=CHCH=CHC(=CH_2)−$RuCl(CO)(PPh_3)_2$, which reacts with *t*-BuNC to give $[(PMe_3)_3(CO)ClRu$−CH=CHCH=CHC(=CH_2)CO−$Ru(t\text{-}BuNC)_3(PPh_3)_2]Cl$.

Introduction

Bimetallic and polymetallic complexes with conjugated hydrocarbon ligands bridging metal centers are attracting considerable interest for their structural and material properties.[1,2] Linear C_x and $(CH)_x$ are probably the simplest hydrocarbon bridging ligands. In the past decade, a variety of complexes of the type $L_nM(\mu\text{-}C_x)\text{-}M'L'_n$ with x up to 20 and with M or M′ = Re, Fe, Ru, Pt, Pd, Mn, W, and Rh have been synthesized.[3−6] These complexes can behave like molecular wires and have luminescent properties. In contrast to bimetallic complexes with C_x bridges, relatively few studies have been carried out on bimetallic complexes with linear $(CH)_x$ bridges. Bimetallic complexes with linear $(CH)_x$ bridges are interesting, as many conjugated organic materials (e.g., polyacetylenes, push/pull stilbenes) have only sp^2-hybridized carbons in their backbones.[7] Until now, only a few examples of $(CH)_x$-bridged bimetallic complexes where $x = 2$,[8] 4,[9−11] 5,[12] and 6[13] have been reported.

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(1) (a) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21, and references therein. (b) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969. (c) Lotz, S.; Van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995**, *37*, 219. (d) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (e) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. (f) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923. (g) Paul, F.; Lapinte, C. *Coord. Chem.* **1998**, *178*, 431.

(2) For examples of recent work, see: (a) Hurst, S. K.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2002**, *21*, 2353. (b) Hurst, S. K.; Humphrey, M. K.; Isoshima, T.; Wostyn, K.; Asselberghs, I.; Clay, K.; Persoons, A.; Samoc, M.; Luther-Davies, B. *Organometallics* **2002**, *21*, 2024. (c) Enriquez, A. E.; Templeton, J. L. *Organometallics* **2002**, *21*, 852. (d) Yam, V. W. W.; Tao, C. H.; Zhang, L.; Wong, K. M. C.; Cheung, K. K. *Organometallics* **2001**, *20*, 453. (e) Matsumi, N.; Chujo, Y.; Lavastre, O.; Dixneuf, P. H. *Organometallics* **2001**, *20*, 2425. (f) Altamura, P.; Giardina, G.; Lo Sterzo, C.; Russo, M. V. *Organometallics* **2001**, *20*, 4360. (g) Wong, W. Y.; Choi, K. H.; Lu, G. L.; Shi, J. X.; Lai, P. Y.; Chan, S. M.; Lin, Z. *Organometallics* **2001**, *20*, 5446. (h) Le Stang, S.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 1035. (i) Weyland, T.; Costuas, K.; Toupet, L.; Halet, J. F.; Lapinte, C. *Organometallics* **2000**, *19*, 4228. (j) Weyland, T.; Ledoux, I.; Brasselet, S.; Zyss, J.; Lapinte, C. *Organometallics* **2000**, *19*, 5235. (k) MacDonald, M. A.; Puddephatt, R. J.; Yap, G. P. A. *Organometallics* **2000**, *19*, 2194.

(3) (a) Meyer, W. E.; Amoroso, A. J.; Horn, C. R.; Jaeger, M.; Gladysz, J. A. *Organometallics* **2001**, *20*, 1115. (b) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *112*, 810. (c) Brady, M.; Weng, W.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2665.

(4) (a) Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 3719. (b) Bruce, M. I.; Kelly, B. D.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *604*, 150.

(5) Lu, W.; Xiang, H. F.; Zhu, N.; Che, C. M. *Organometallics* **2002**, *21*, 2343.

(6) For additional examples of bimetallic complexes with C_x bridges, see for example: (a) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Inorg. Chem.* **2001**, *40*, 3263. (b) Che, C. M.; Chao, H. Y.; Miskowski, V. M.; Li, Y.; Cheung, K. K. *J. Am. Chem. Soc.* **2001**, *123*, 4895. (c) Paul, F.; Meyer, W. E.; Toupet, L.; Jiao, H.; Gladysz, J. A.; Lapinte, C. *J. Am. Chem. Soc.* **2000**, *122*, 9405. (d) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J. F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949. (e) Gil-Rubio, J.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 1365. (f) Peters, T. B.; Bohling, J. C.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1999**, *18*, 3261. (g) Sakurai, A.; Akita, M.; Moro-oka, Y. *Organometallics* **1999**, *18*, 3241. (h) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539. (i) Akita, M.; Chung, M. C.; Sakurai, A.; Sugimoto, S.; Terada, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4882. (j) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477.

(7) See for example: (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195, and references therein. (b) Bredas, J. L.; Adant, C.; Tackx, P.; Peraoons, A. *Chem. Rev.* **1994**, *94*, 243. (c) *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Maecel Dekker: New York, 1998.

(8) (a) Rajapakse, N.; James, B. R.; Dolphin, D. *Can. J. Chem.* **1990**, *68*, 2274. (b) Bullock, R. M.; Lemke, F. R.; Szalda, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 3244. (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466.

(9) (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) Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 2221.

10.1021/om0207663 CCC: \$25.00
Publication on Web 01/18/2003

Other reported bimetallic complexes with hydrocarbon bridges containing only sp^2-hybridized carbons in the backbone include bimetallic complexes of the type $L_nM{=}C(OR){-}CH{=}CH{-}C(OR){=}ML_n$ or $L_nM{=}CR{-}R{-}CR{=}ML_n$,[14] $L_nM{-}Ar{-}ML_n$,[15] $L_nMCH{=}CH{-}Ar{-}CH{=}CHML_n$,[16] and $L_nM{-}C_4R_3{-}ML_n$.[17]

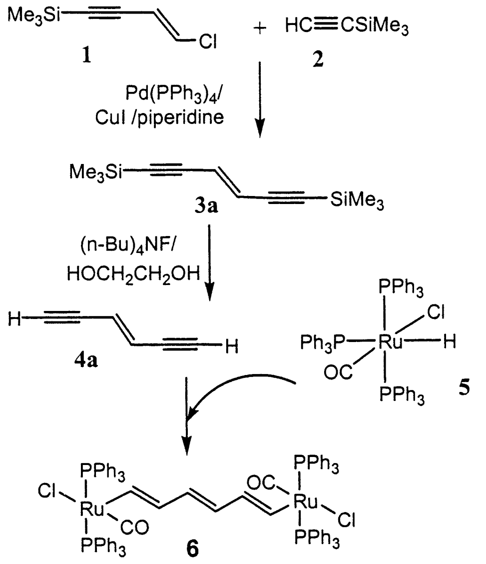
In this report, the synthesis, characterization, and electrochemical properties of several $(CH)_6$-bridged bimetallic complexes will be described. Reported bimetallic complexes with a $(CH)_6$ bridge are limited to $(S)(RO)_2(ArN)Mo{=}CH{-}(CH{=}CH)_2{-}CH{=}MoNAr)(OR)_2(S)$ ($RO = OCMe(CF_3)_2$; Ar = 2,6-diisopropylphenyl; $S = MeOCH_2CH_2OMe$, ether, THF), which were derived from the reactions of $Mo(CHR')(NAr)(OR)_2$ ($R' = CMe_3$, CMe_2Ph) with cyclooctatetrene.[13]

Results and Discussion

Reactions of (*E*)-HC≡CCH=CHC≡CH with RuHCl(CO)(PPh$_3$)$_3$. Reactions of $RuHCl(CO)(PPh_3)_3$ with $HC{\equiv}CR$ are known to give $RuCl((E){-}CH{=}CHR)(CO)(PPh_3)_2$.[18,19] Thus it is expected that reactions of $RuHCl(CO)(PPh_3)_3$ with (*E*)-$HC{\equiv}CCH{=}CHC{\equiv}CH$ will produce $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}(E,E,E){-}CH{=}CHCH{=}CHCH{=}CH)$.

The starting material (*E*)-$HC{\equiv}CCH{=}CHC{\equiv}CH$ (**4a**) was initially prepared from the reaction of *p*-toluenesulfonate of hexa-1,5-diyn-3-ol with diazabicyclo[4.3.0]non-5-ene.[20] The reaction produces a mixture of (*E*)- and (*Z*)-$HC{\equiv}CCH{=}CHC{\equiv}CH$, which are difficult to separate. We have generated the compound (*E*)-$HC{\equiv}CCH{=}CHC{\equiv}CH$ (**4a**) by desilylation of (*E*)-$Me_3SiC{\equiv}CCH{=}CHC{\equiv}CSiMe_3$ (**3a**), a method reported by Wudl et al.[21] (*E*)-$Me_3SiC{\equiv}CCH{=}CHC{\equiv}CSiMe_3$ (**3a**) was in turn synthesized from Pd-catalyzed coupling reaction of (*E*)-$ClCH{=}CHC{\equiv}CSiMe_3$ (**1**)[22] and $HC{\equiv}CSiMe_3$ (**2**) (Scheme 1). The one-pot reaction of (*E*)-$ClCH{=}CHCl$ and $HC{\equiv}CSiMe_3$ could also generate **3a**. However, significant amounts of side-products such as (*Z*)-$Me_3SiC{\equiv}CCH{=}CHC{\equiv}CSiMe_3$ (**3b**) and $Me_3SiC{\equiv}CCH{=}CHC({=}CHSiMe_3)C{\equiv}CSiMe_3$ were also produced in the reaction.[23]

Scheme 1



Addition of **4a** to a suspension of $RuHCl(CO)(PPh_3)_3$ (**5**) in dichloromethane produced the insertion product $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}(E,E,E){-}CH{=}CHCH{=}CHCH{=}CH)$ (**6**), which can be isolated as a purple solid in 81% yield (Scheme 1). The compound has been characterized by NMR and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed a singlet at 29.5 ppm, which is typical for $RuCl((E){-}CH{=}CHR)(CO)(PPh_3)_2$. The ^1H NMR spectrum in CD_2Cl_2 displayed the Ru-CH signal at 7.94 ppm, the β-CH signal at 5.39 ppm, and the δ-CH signal at 5.21 ppm. Monomeric complexes $RuCl(RC{=}CHR')(CO)(PPh_3)_2$ are known to adopt a distorted trigonal bipyramidal geometry around ruthenium with the two PPh_3 ligands in the apical positions.[18] Thus it is reasonable to assume that complex **6** has a similar geometry around ruthenium. Reported bimetallic complexes closely related to **6** are $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}Ar{-}CH{=}CH)$[16a,b] and $[RuCl(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CH{-}CH{=}CH)$.[11]

Reactions of 6 with PMe$_3$, 4-Phenylpyridine, PMP, and *t*-BuNC. Several bimetallic complexes were prepared from complex **6**. Treatment of **6** with PMe_3 produced the six-coordinated complex $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CH)$ (**7**) (Scheme 2). The PMe_3 ligands in **7** are meridionally coordinated to ruthenium as indicated by the AM_2 pattern $^{31}P\{^1H\}$ NMR spectrum. The presence of the $(CH)_6$ chain is indicated by the ^1H NMR spectrum (in CD_2Cl_2), which showed the vinyl proton signals at 7.75 (Ru-CH), 6.88

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[10] Niu, X.; Gopal, L.; Masingale, M. P.; Braden, D. A.; Hudson, B. S.; Sponsler, M. B. *Organometallics* **2000**, *19*, 649.

[11] Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1998**, *17*, 4762.

[12] (a) Xia, H. P.; Jia, G. *Organometallics* **1997**, *16*, 1. (b) Xia, H. P.; Yeung, R. C. Y.; Jia, G. *Organometallics* **1997**, *16*, 3557.

[13] Fox, H. H.; Lee, J. K.; Park, L. Y.; Schrock, R. R. *Organometalics* **1993**, *12*, 759.

[14] See for example: (a) Guillaume, V.; Mahias, V.; Mari, A.; Lapinte, C. *Organometallics* **2000**, *19*, 1422. (b) Fernández, I.; Sierra, M. A.; Mancheño, M. J.; Gómez-Gallego, M.; Ricart, S. *Organometallics* **2001**, *20*, 4304. (c) Ulrich, K.; Guerchais, V.; Dötz, K. H.; Toupet, L.; Le Bozec, H. *Eur. J. Inorg. Chem.* **2001**, 725. (d) Rabier, A.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **2001**, *617*, 681. (e) Briel, O.; Fehn, A.; Beck, W. *J. Organomet. Chem.* **1999**, *578*, 247.

[15] See for example: (a) Dijkstra, H. P.; Albrecht, M.; van Koten, G. *Chem. Commun.* **2002**, 126. (b) Dijkstra, H. P.; Meijer, M. D.; Patal, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Canty, A. J.; van Koten, G. *Organometallics* **2001**, *20*, 3159. (c) Lagunas, M. C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731. (d) Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J. *Organometallics* **1997**, *16*, 1897.

[16] (a) Gómez-Lor, B.; Santos, A.; Ruiz, M.; Echavarren, A. M. *Eur. J. Inorg. Chem.* **2001**, 2305. (b) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. P. *J. Organomet. Chem.* **1997**, *539*, 53. (c) Santos, A.; López, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren A. M. *Organometallics* **1994**, *13*, 3605.

[17] See for example: (a) Weng, W.; Bartik, T.; Johnson, M. T.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 889. (b) Fischer, H.; Leroux, F.; Roth, G.; Stumpf, R. *Organometallics* **1996**, *15*, 3723, and references therein.

[18] Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169.

[19] For recent work, see for example: (a) Maruyama, Y.; Yamamura, K.; Sagawa, T.; Katayama, H.; Ozawa, F. *Organometallics* **2000**, *19*, 1308. (b) Maruyama, Y.; Yamamura, K.; Nakayama, I.; Yoshiuchi, K.; Ozawa, F. *J. Am. Chem. Soc.* **1998**, *120*, 1421. (c) Harlow, K. J.; Hill, A. F.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1999**, 1911. (d) Hill, A. F.; Ho, C. T.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1997**, 2207. (e) Harlow, K. J.; Hill, A. F.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **1998**, *17*, 1916. (f) Jia, G.; Wu, W. F.; Yeung, R. C. Y.; Xia, H. *J. Organomet. Chem.* **1997**, *538*, 31.

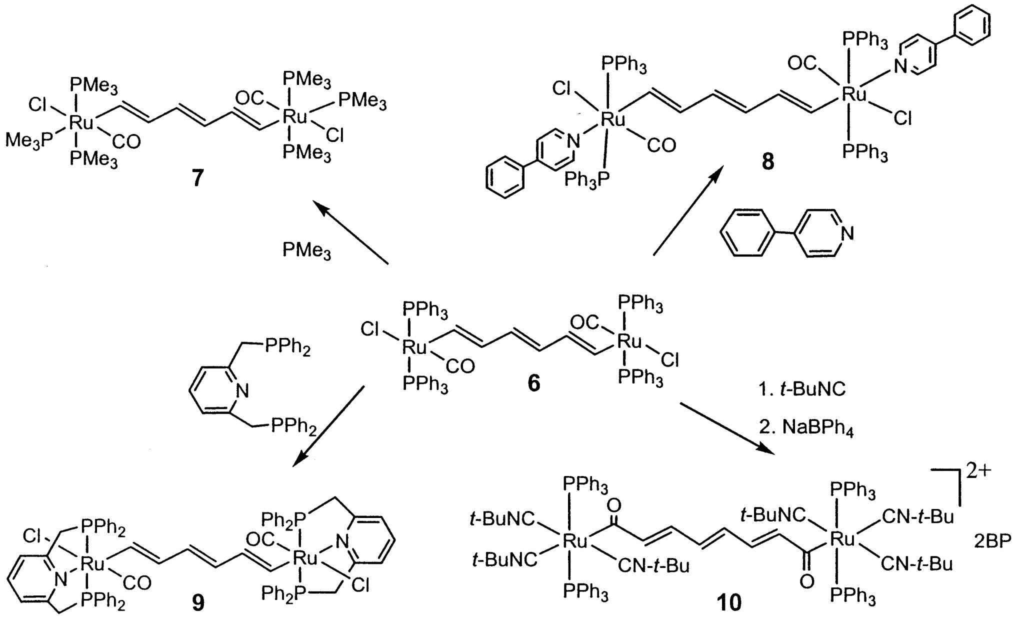
[20] (a) Okamura, W. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 5991. (b) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

[21] Walker, J. A.; Bitler, S. P.; Wudl, F. *J. Org. Chem.* **1984**, *49*, 4733.

[22] Chemin, D.; Linstrumelle, G. *Tetrahedron* **1994**, *50*, 5335.

[23] Vollhardt, K. P. C.; Win, L. S. *Tetrahedron Lett.* **1985**, *709*, 712.

Scheme 2



(β-CH), and 6.52 (γ-CH) ppm. In the $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2), the CH signals were observed at 166.6 (Ru-CH), 138.4 (β-CH), and 129.4 (γ-CH) ppm. The vinyl group is trans to the unique PMe_3, as indicated by the large $^2J(PC)$ coupling constant (75.5 Hz).

Reactions of **6** with 4-phenylpyridine and 2,6-$(Ph_2PCH_2)_2C_5H_3N$ (PMP) give the corresponding six-coordinated complexes $[RuCl(PhPy)(CO)(PPh_3)_2]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CH)$ (**8**) and $[RuCl(CO)(PMP)]_2(\mu\text{-}CH{=}CHCH{=}CHCH{=}CH)$ (**9**), respectively. These complexes have been characterized by NMR spectroscopy and elemental analysis. Related mononuclear complexes $RuCl(CH{=}CHR)(L)(CO)(PPh_3)_2$ (L = 2e nitrogen donor ligands) have been previously prepared from the reaction of $HC{\equiv}CR$ with $RuHCl(L)(CO)(PPh_3)_2$.[24] Ruthenium PMP complexes, for example, $RuCl_2(PPh_3)(PMP)$ and $RuHX(PPh_3)(PMP)$ (X = Cl, OAc), have been reported recently.[25]

Complex **6** reacted with *t*-BuCN to give the bimetallic complex $\{[Ru(BuCN)_3(PPh_3)_2]_2(\mu\text{-}COCH{=}CHCH{=}CHCH{=}CHCO)\}^{2+}$, which was isolated as the BPh_4 salt **10** by treatment of the crude product with $NaBPh_4$ (Scheme 2). The compound has been characterized by NMR spectroscopy and elemental analysis. The presence of the COCH=CHCH=CHCH=CHCO bridging ligand is supported by the ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ^1H NMR spectrum (in CD_2Cl_2), the three olefinic signals were observed at 5.28, 5.56, and 5.69 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the Ru-acyl signal was observed at 260.2 ppm and the CO*C*H signal was observed at 142.2 ppm. The other two CH signals were observed at 126.1 (δ-CH) and 137.6 (γ-CH) ppm. For comparison, the ^{13}C signal for the acyl carbon was observed at 260.5 ppm for $[Ru(COPh)(t\text{-}BuNC)_2(CO)(PMe_2Ph)_2]^+$ [26] and at 258.1 ppm for $[Ru(COCH{=}CHCMe_3)(t\text{-}BuNC)_3(PPh_3)_2]^+$.[27]

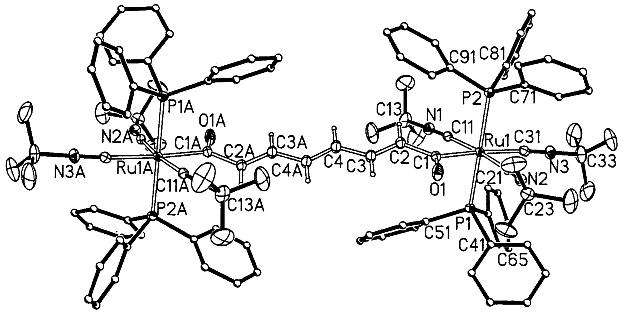


Figure 1. Molecucular structure of the complex ion $\{[Ru(t\text{-}BuNC)_3(PPh_3)_2]_2(\mu\text{-}COCH{=}CHCH{=}CHCH{=}CHCO)\}^{2+}$. The counteranion and the hydrogen atoms of PPh_3 and *t*-BuNC are omitted for clarity.

The structure of **10** has been confirmed by X-ray diffraction. The molecular structure of the complex ion of **10** is depicted in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively. As shown in Figure 1, the compound contains two ruthenium centers linked by a COCH=CHCH=CHCH=CHCO bridge. The two ruthenium centers are related to each other by an inversion center at the midpoint of the C4−C4A bond. The geometry around ruthenium can be described as a distorted octahedron with three meridionally bound *t*-BuCN ligands, two trans-disposed PPh_3 ligands, and an acyl ligand trans to the unique *t*-BuCN ligand, as suggested by the solution NMR data. The unique Ru−C(31) bond (2.038(4) Å) is slightly longer than those of the mutually trans Ru−C (isonitrile) bonds (1.980(3) and 1.996(3) Å), probably due to the strong trans influence of the acyl ligand.

The most interesting features of the structure are those related to the COCH=CHCH=CHCH=CHCO

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[24] (a) Santos, A.; López, J.; Galán, A.; González, J. J.; Tinoco, P.; Echavarren, A. M. *Organometallics* **1997**, *16*, 3482. (b) Romereo, A.; Santos, A.; López, J.; Echavarren, A. M. *J. Organomet. Chem.* **1990**, *391*, 219.

[25] (a) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, *16*, 3941. (b) Rahmouni, N.; Osborn, J. A.; De Cian, A.; Fischer, J.; Ezzamarty, A. *Organometallics* **1998**, *17*, 2470, and references therein.

[26] Dauter, Z.; Mawby, R.; Reynolds, C. D.; Saunders, D. R. *J. Chem. Soc., Dalton Trans.* **1987**, 27.

[27] Montoya, J.; Santos, A.; López, J.; Echavarren, A. M.; Ros, J.; Romero, A. *J. Organomet. Chem.* **1992**, *426*, 383.

Table 1. Crystal Data and Structure Refinement for {[Ru(*t*-BuNC)$_3$(PPh$_3$)$_2$]$_2$-(μ-COCH=CHCH=CHCH=CHCO)}(BPh$_4$)$_2$·6CH$_2$Cl$_2$

formula	$C_{158}H_{160}B_2N_6O_2P_4Ru_2 \cdot 6CH_2Cl_2$
fw	3032.12
cryst syst	monoclinic
space group	$P2(1)/c$
a, Å	12.2869(16)
b, Å	17.200(2) Å
c, Å	38.490(5) Å
β, deg	99.158(3)
V, Å^3	8030.7(18) Å^3
Z	2
D_{calc}, g cm^{-3}	1.254
abs coeff, mm^{-1}	0.479
F(000)	3152
θ range, deg	1.84 to 27.56
index ranges	$-15 \le h \le 15$, $-19 \le k \le 22$, $-50 \le l \le 43$
no. of reflns collected	54 071
no. of ind reflns	18450 [R(int) = 0.0659]
completeness to θ = 27.56°	99.5%
no. of obsd reflns [$I > 2\sigma(I)$]	9177
max. and min. transmn	1.0000 and 0.8265
no. of data/restraints/params	18450/0/865
goodness-of-fit on F^2	0.877
final R indices [$I > 2\sigma(I)$]	R1 = 0.0500, wR2 = 0.1054
R indices (all data)	R1 = 0.1173, wR2 = 0.1240
largest diff peak and hole	0.742 and −0.582 e·Å^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) for {[Ru(*t*-BuNC)$_3$(PPh$_3$)$_2$]$_2$-(μ-COCH=CHCH=CHCH=CHCO)}(BPh$_4$)$_2$·6CH$_2$Cl$_2$

Bond Distances			
Ru(1)−P(1)	2.3799(9)	Ru(1)−P(2)	2.3682(9)
Ru(1)−C(1)	2.118(3)	Ru(1)−C(11)	1.980(3)
Ru(1)−C(21)	1.996(3)	Ru(1)−C(31)	2.038(4)
O(1)−C(1)	1.224(4)	C(1)−C(2)	1.494(4)
C(2)−C(3)	1.322(4)	C(3)−C(4)	1.433(4)
C(4)−C(4)#1	1.334(6)	C(11)−N(1)	1.156(4)
N(1)−C(13)	1.454(4)	C(21)−N(2)	1.151(4)
N(2)−C(23)	1.460(4)	C(31)−N(3)	1.155(4)
N(3)−C(33)	1.462(5)		

Bond Angles			
P(2)−Ru(1)−P(1)	175.43(3)	C(31)−Ru(1)−C(1)	171.72(13)
C(11)−Ru(1)−C(21)	171.55(12)	C(11)−Ru(1)−C(1)	89.81(13)
C(21)−Ru(1)−C(1)	81.76(13)	C(11)−Ru(1)−C(31)	98.41(13)
C(21)−Ru(1)−C(31)	90.00(13)	C(1)−Ru(1)−P(1)	91.45(9)
C(1)−Ru(1)−P(2)	91.34(9)	C(11)−Ru(1)−P(1)	86.53(9)
C(11)−Ru(1)−P(2)	89.86(9)	C(21)−Ru(1)−P(1)	92.97(9)
C(21)−Ru(1)−P(2)	91.01(9)	C(31)−Ru(1)−P(1)	88.02(9)
C(31)−Ru(1)−P(2)	89.73(9)	O(1)−C(1)−Ru(1)	122.7(2)
O(1)−C(1)−C(2)	115.2(3)	C(2)−C(1)−Ru(1)	122.0(2)
C(3)−C(2)−C(1)	122.2(3)	C(2)−C(3)−C(4)	126.6(3)
C(4)#1−C(4)−C(3)	125.0(4)	N(1)−C(11)−Ru(1)	177.0(3)
N(2)−C(21)−Ru(1)	173.0(3)	N(3)−C(31)−Ru(1)	173.7(3)

bridge. The Ru−C(1) bond distance of 2.118(3) Å is close to those found in η^1-acyl complexes such as Ru(Cp)(COCH=CPh$_2$)(CO)(P(*i*-Pr)$_3$) (2.060(2) Å),[28] [Ru(COPh)(CO)(*t*-BuCN)$_2$(PMe$_2$Ph)$_2$]$^+$ (2.128(10) Å),[26] and [Ru(COMe)(cym)(phen)]BAr$_4$ (2.084(11) Å, cym = 4-methylisopropylbenzene, phen = phenanthroline, Ar = 3,5-bis(trifluoromethyl)phenyl)[29] and is slightly longer than that found in the η^2-acyl complex RuCl(η^2-COC$_6$H$_4$NH$_2$)(CO)(PPh$_3$)$_2$ (1.958(3) Å).[30] The atoms Ru, C(11), C(21), C(31), C(1), and O(1) are essentially coplanar with maximum deviation from the least-squares plane of 0.022 Å for O(1). The carbon atoms of the COCH=CHCH=CHCH=CHCO chain and the ruthenium atoms are also essentially coplanar with maximum deviation from the least-squares plane of 0.026 Å for C(3). The two planes have a dihedronal angle of 30.6°, indicating that the π-conjugation in the chain is not very effective. The coplanarity of the acyl group (C(1)O(1)) and the isonitrile ligands is probably due to the fact that these ligands are both good π-acceptors and stabilization due to π-interaction of isonitrile and acyl group with the metal centers can be maximized in such a conformation. A similar argument has been proposed for the conformational preferences of vinyl groups in CO-containing vinyl complexes M(CR=CR′R′)(CO)L$_n$.[31]

The (CH)$_6$ ligand shows a single/double carbon−carbon bond alternation. All the olefinic double bonds are in trans geometry. The formal C=C double bonds have an average bond distance of 1.328 Å, and the formal single bond (C(3)−C(4) has a bond distance of 1.433(4) Å, which is slightly shorter than that (1.494(4) Å) between C(2) and C(1) (the acyl carbon). The difference between the single and the average double bond distances of the (CH)$_6$ chain is 0.105 Å. The structural parameters of the (CH)$_6$ chain are similar to those of PhCH=CH(CH=CH)$_2$CH=CHPh,[32] where the difference between the average single and double bond distances is 0.092 Å.

As mentioned previously, reported (CH)$_6$-bridged bimetallic complexes are limited to (S)(RO)$_2$(ArN)Mo=CH−(CH=CH)$_2$−CH=MoNAr)(OR)$_2$(S) (RO = OCMe(CF$_3$)$_2$; Ar = 2,6-diisopropylphenyl; S = MeOCH$_2$CH$_2$OMe, ether, THF), which were derived from the reactions of Mo(CHR′)(NAr)(OR)$_2$ (R′ = CMe$_3$, CMe$_2$Ph) with cyclooctatetrene.[13] Several C$_6$-bridged bimetallic complexes have been reported, including, Cp*(dppe)Fe−(C≡C)$_3$−Fe(dppe)Cp*,[1g] Cp*(NO)(PR$_3$)Re−(C≡C)$_3$−Re(NO)(PR$_3$)Cp* (PR$_3$ = PPh$_3$, P(tolyl)$_3$),[3] Cp(PPh$_3$)$_2$Ru−(C≡C)$_3$−Ru(PPh$_3$)$_2$Cp,[4] and Cy$_3$PAu−(C≡C)$_3$−AuPCy$_3$.[5]

Reactions of (*Z*)-HC≡CCH=CHC≡CH with RuHCl(CO)(PPh$_3$)$_3$. For comparison, we have also attempted to prepare analogous bimetallic complexes using (*Z*)-HC≡CCH=CHC≡CH (**4b**) instead of (*E*)-HC≡CCH=CHC≡CH (**4a**). Compound **4b** was generated by desilylation of (*Z*)-Me$_3$SiC≡CCH=CHC≡CSiMe$_3$ (**3b**), a method recently reported by McMahon et al.[33]

Surprisingly, the expected bimetallic complex could not be produced in the reaction of RuHCl(CO)(PPh$_3$)$_3$ with 0.5 equiv of **4b**. As indicated by the ^{1}H and ^{31}P{^{1}H} NMR spectra, the reaction produced a complicated mixture, which was difficult to purify and identify. To better understand the reaction, the reaction of RuHCl(CO)(PPh$_3$)$_3$ with excess **4b** was carried out. An in situ ^{31}P{^{1}H} NMR experiment suggests that the mononuclear complex RuCl((*E*,*Z*)-CH=CHCH=CHC≡CH)(CO)(PPh$_3$)$_2$ was generated in the reaction. However, the compound is unstable and could be isolated in pure state. On the other hand, reaction of RuHCl(CO)(PPh$_3$)$_3$ with excess **4b** followed by treatment of the reaction mixture with PMe$_3$ produced the six-coordinated com-

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[28] Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

[29] Menéndez, C.; Morales, D.; Pérez, J.; Riera, V.; Miguel, D. *Organometallics* **2001**, *20*, 2775.

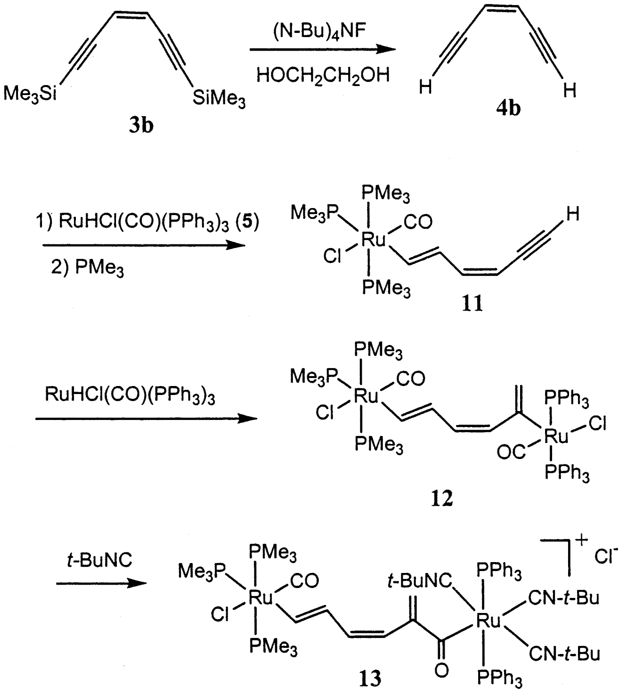
[30] Clark, G. R.; Roper, W. R.; Wright, L. J.; Yap, V. P. *Organometallics* **1997**, *16*, 5135.

[31] Choi, S. H.; Bytheway, I.; Lin, Z.; Jia, G. *Organometallics* **1998**, *17*, 3974.

[32] Drenth, W.; Wiebenga, E. H. *Acta Crystallogr.* **1955**, *8*, 755.

[33] McMahon, R. J.; Halter, R. J.; Fimmen, R. L.; Wilson, R. J.; Peebles, S. A.; Kuczkowski, R. L.; Stanton, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 939.

Scheme 3



plex Ru((*E*,*Z*)-CH=CHCH=CHC$\equiv$CH)Cl(CO)(PMe$_3$)$_3$ (**11**, see Scheme 3). Compound **11** has been characterized by multinuclear NMR and elemental analysis. The ^{31}P{^{1}H} NMR spectrum in CD$_2$Cl$_2$ showed a doublet at -9.3 ppm and a triplet at -20.6 ppm, indicating that the three PMe$_3$ ligands are meridionally coordinated to ruthenium. In the ^{1}H NMR spectrum (in CD$_2$Cl$_2$), the signals of the CH=CHCH=CHC$\equiv$CH group are observed at 8.16 (Ru-CH), 6.99 (β-CH), 6.48 (γ-CH), 4.89 (δ-CH), and 3.20 ($\equiv$CH) ppm. In the ^{13}C{^{1}H} NMR spectrum (in CD$_2$Cl$_2$), the signals of the CH=CHCH=CHC$\equiv$CH group were observed at 185.1 (Ru-CH), 147.0 (β-CH), 134.9 (γ-CH), and 94.1 (δ-CH), 82.8 ($\equiv$C), and 78.9 ($\equiv$CH) ppm. The vinyl group is trans to the unique PMe$_3$, as indicated by the large ^2J(PC) coupling constant (77.5 Hz).

Preparation of Bimetallic Complexes from RuCl((*E*,*Z*)-CH=CHCH=CHC$\equiv$CH)(CO)(PMe$_3$)$_3$ (11). We have tried to use compound **11** as the starting material to prepare bimetallic complexes. It is expected that reaction of **11** with RuHCl(CO)(PPh$_3$)$_3$ would produce the bimetallic complex (PMe$_3$)$_3$(CO)ClRu$-$(*E*,*Z*,*E*)-CH=CHCH=CHCH=CH$-$RuCl(CO)(PPh$_3$)$_2$. Treatment of compound **11** with 1 equiv of RuHCl(CO)(PPh$_3$)$_3$ produced, unexpectly, the bimetallic complex (PMe$_3$)$_3$(CO)ClRu$-$(*E*,*Z*)-CH=CHCH=CHC(=CH$_2$)$-$RuCl(CO)(PPh$_3$)$_2$ (**12**), rather than (PMe$_3$)$_3$(CO)ClRu$-$(*E*,*Z*,*E*)-CH=CHCH=CHCH=CHRuCl(CO)(PPh$_3$)$_2$ (Scheme 3). The reaction is unusual because reactions of RuHCl(CO)(PPh$_3$)$_3$ with RC$\equiv$CH normally give RuCl(CH=CHR)(CO)(PPh$_3$)$_2$, rather than RuCl(CR=CH$_2$)(CO)(PPh$_3$)$_2$. It is not clear to us why ruthenium is not attached to the terminal carbon in the insertion reaction.

The formation of the bimetallic complex is confirmed by elemental analysis and NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum in CD$_2$Cl$_2$ showed a singlet for the PPh$_3$ ligand at 30.5 ppm and AM2 pattern PMe$_3$ signals at -20.7 (t, J(PP) $= 23.1$ Hz) and -9.0 ppm (d, J(PP) $=$ 23.1 Hz). The presence of the CH=CHCH=CHC(=CH$_2$) group is supported by the ^{1}H NMR spectrum (in CD$_2$Cl$_2$), which showed a characteristic doublet signal at 5.96 ppm for =C*H*C=CH$_2$.

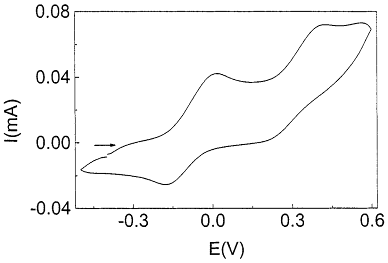


Figure 2. Cyclic voltammogram of [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CHCH=CH$-$CH=CH).

Further support for the structural assignment is from its reaction with *t*-BuNC. Reaction of complex **12** with *t*-BuNC produced [(PMe$_3$)$_3$(CO)ClRuCH=CHCH=CHC(=CH$_2$)CORu(*t*-BuNC)$_3$(PPh$_3$)$_2$]Cl (**13**). The presence of the CH=CHCH=CHC(=CH$_2$)CO bridging ligand is clearly indicated by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In the ^{13}C{^{1}H} NMR spectrum, the Ru-acyl signal was observed at 257.2 ppm. In the ^{1}H NMR spectrum, the =CH$_2$ signals was observed at 4.90(s) and 5.30(s) ppm, and the other four ^{1}H signals of the bridging ligand were observed at 5.06 (d, J(HH) $= 11.8$ Hz, δ-CH), 5.90 (t, J(HH) $= 11.8$ Hz, γ-CH), 6.67 (m, β-CH), and 7.85 (m, Ru-CH) ppm. It is interesting to note that only one side of the metal center undergoes CO insertion reaction.

Electrochemical Study. Electrochemistry can often be used to probe metal$-$metal interactions in bimetallic complexes with σ,σ-bridging hydrocarbon chains.[1g] Electrochemical properties of bimetallic complexes with C$_x$ bridges have been extensively studied by cyclic voltammetry. In contrast, electrochemical properties of bimetallic complexes with (CH)$_x$ bridges have rarely been exploited. In this work, we have collected cyclic voltammograms of complexes **6**$-$**9** in dichloromethane containing 0.10 M *n*-Bu$_4$NClO$_4$ as the supporting electrolyte.

The five-coordinated complex **6** exhibited two partially reversible oxidation waves at 0.15 and -0.15 V vs Ag/AgCl. These two waves can be attributed to the formation of [(PPh$_3$)$_2$(CO)ClRu$-$(CH=CH)$_3$$-$RuCl(CO)(PPh$_3$)$_2$]$^+$ and [(PPh$_3$)$_2$(CO)ClRu=CH$-$(CH=CH)$_2$$-$CH=RuCl(CO)(PPh$_3$)$_2$]$^{2+}$, respectively. The peak separation of the two oxidation waves is at 0.30 V.

The cyclic voltammograms of the six-coordinated complexes **7**$-$**9** have features very similar to those of **6**. As an example, the cyclic voltammogram of **7** is presented in Figure 2. As shown in Figure 2, the PMe$_3$-containing complex **7** showed two partially reversible oxidation waves at -0.07 and 0.31 V vs Ag/AgCl. The pyridine-containing complexes **8** and **9** can be oxidized more easily compared to the PMe$_3$-containing complex **7**. Complex **8** showed two partially reversible oxidation waves at -0.22 and 0.16 V vs Ag/AgCl. Complex **9** showed two partially reversible oxidation waves at -0.26 and 0.09 V vs Ag/AgCl. The two waves observed for **7**$-$**9** can be attributed to the formation of [L$_5$Ru$-$(CH=CH)$_3$$-RuL_5$]$^+$ and [L$_5$Ru=CH$-$(CH=CH)$_2$$-$CH=RuL$_5$]$^{2+}$, respectively. The peak separations of the two oxidation waves for complexes **7**, **8**, and **9** are at 0.38, 0.38, and 0.35 V, respectively. Observation of two oxidation waves for complexes **6**$-$**9** may imply that the two metal centers can interact with each other. For comparison, the peak separation for the $(CH)_4$-bridged complex Cp(dppm)Fe$-$(CH$=$CH)$_2-$Fe(dppm)Cp is at 0.44 V.[14b]

The electrochemical properties of C_6-bridged bimetallic complexes such as Cp*(dppe)Fe$-(C\equiv C)_3-$Fe(dppe)Cp*[1g] and Cp*(NO)(PR$_3$)Re$-(C\equiv C)_3-$Re(NO)(PR$_3$)Cp*[3] have been reported. The complex Cp*(dppe)Fe$-(C\equiv C)_3-$Fe(dppe)Cp* exhibits two oxidation waves at -0.42 and 0.11 V vs SCE with a peak separation of 0.53 V; the complex Cp*(NO)(PPh$_3$)Re$-(C\equiv C)_3-$Re(NO)(PPh$_3$)Cp* exhibits two oxidation waves at 0.10 and 0.48 V vs SCE with a peak separation of 0.38 V; the complex Cp*(NO)(P(tolyl)$_3$)Re$-(C\equiv C)_3-$Re(NO)(P(tolyl)$_3$)Cp* exhibited two oxidation waves at 0.02 and 0.41 V vs SCE with a peak separation of 0.39 V. It appears that both C_6 and $(CH)_6$ bridges can mediate electronic communication between the two metal centers. However, the relative effectiveness of $(CH)_6$ and C_6 in the mediation of electronic communication between metal centers could not be evaluated just based the CV data of our $(CH)_6$-bridged complexes and those of reported C_6-bridged complexes, because the peak separations in cyclic voltammograms are also dependent on metals as well as other ligands.

Experimental Section

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane, $CHCl_3$). The starting materials RuHCl(CO)(PPh$_3$)$_3$,[34] (1*E*)-1-chloro-4-(trimethylsilyl)but-1-en-3-yne,[22] and 2,6-(Ph$_2$PCH$_2$)$_2$C$_5$H$_3$N (PMP)[35] were prepared according to literature methods. (*E*)-Me$_3$SiC$\equiv$CCH$=$CHC$\equiv$CSiMe$_3$[21] and (*Z*)-Me$_3$SiC$\equiv$CCH$=$CHC$\equiv$CSiMe$_3$[33] were prepared by modified literature methods. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were collected on a Bruker ARX-300 spectrometer (300 MHz). ^{1}H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

The electrochemical measurements were performed with a PAR model 273 potentiostat. A three-component electrochemical cell was used with a glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The cyclic voltammograms were collected with a scan rate of 100 mV/s in CH_2Cl_2 containing 0.10 M *n*-Bu$_4$NClO$_4$ as the supporting electrolyte. The peak potentials reported are referenced to Ag/AgCl. The ferrocene/ferrocenium redox couple was located at 0.26 V under our experimental conditions.

(*E*)-1,6-Bis(trimethylsilyl)hex-3-ene-1,5-diyne (3a). A solution of trimethylsilylacetene (4.0 g, 41 mmol) in benzene (15 mL) was slowly added to a mixture of (1*E*)-1-chloro-4-(trimethylsilyl)but-1-en-3-yne (**1**) (6.5 g, 41 mmol), Pd(PPh$_3$)$_4$ (3.0 g, 2.6 mmol), and CuI (0.92 g, 4.8 mmol) in piperidine (12 mL). The reaction mixture was stirred for 3 h. The reaction was then quenched with a saturated aqueous solution of NH_4Cl (80 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL), dried over $MgSO_4$, and filtered. The solvents were removed by rotary evaporation to yield a brown oil. A pentane/ether solution (1:1; 100 mL) was added, and the precipitate formed was removed by filtration. The solvents of the filtrate were removed by rotary evaporation, and the resulting brown oil was further purified by flash column chromatography (silica gel, hexane) to give a yellow solid. Yield: 5.5 g, 61%. The compound is pure as judged by its NMR data. The moderate yield is due to loss in purification. ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 0.26 (s, 18 H, SiMe$_3$), 6.19 (s, 2 H, HC$=$CH). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz): δ -0.62 (s, SiMe$_3$), 100.5 (s, C$\equiv$C), 103.1 (s, C$\equiv$C), 121.7 (s, $=$CH).

[RuCl(CO)(PPh$_3$)$_2$]$_2$(*μ*-(*E*,*E*,*E*)-CH$=$CHCH$=$CHCH$=$CH) (6). Compound **3a** (0.500 g, 2.27 mmol) in THF (5 mL) was slowly added to a mixture of tetra-*n*-butylammonium fluoride (5 mL, 1.0 M in THF) and ethylene glycol (4 mL). The solution was stirred for 3 h at room temperature. Most of the THF was removed by rotary evaporation. The enediyne **4a** was collected from the reaction mixture by vacuum distillation into a liquid nitrogen cooled flask. The collected **4a** was then diluted with CH_2Cl_2 (15 mL). The solution was then slowly added to a suspension of RuHCl(CO)(PPh$_3$)$_3$ (1.50 g, 1.57 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 30 min to give a red solution. The mixture was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 3 mL under vacuum. Addition of hexane (50 mL) to the residue produced a purple solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.92 g, 81%. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz): δ 29.5 (s). ^{1}H NMR (CD$_2$Cl$_2$, 300.13 MHz): δ 5.21 (br, 2 H, γ-CH), 5.39 (br, 2 H, β-CH), 7.41$-$7.73 (m, 60 H, PPh$_3$), 7.94 (br, 2 H, Ru-CH). Anal. Calcd for $C_{80}H_{66}Cl_2O_2P_4Ru_2\cdot 0.5CH_2Cl_2$: C, 64.51; H, 4.51. Found: C, 64.71; H, 5.00.

[RuCl(CO)(PMe$_3$)$_3$]$_2$(*μ*-CH$=$CHCH$=$CHCH$=$CH) (7). To a solution of complex **6** (0.50 g, 0.34 mmol) in CH_2Cl_2 (20 mL) was added 5 mL of a THF solution of PMe$_3$ (1.0 M, 5.00 mmol). The reaction mixture was stirred for 15 h. The volatile materials were removed under vacuum. The solid was redissolved in benzene (3 mL). Addition of hexane (40 mL) to the residue produced a pale yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.23 g, 78%. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.5 MHz): δ -20.6 (t, J(PP) $=$ 22.1 Hz), -8.6 (d, J(PP) $=$ 22.1 Hz). ^{1}H NMR (C$_6$D$_6$, 300.13 MHz): δ 1.12 (d, J(PH) $=$ 6.6 Hz, 18 H, PMe$_3$), 1.22 (t, J(PH) $=$ 3.4 Hz, 36 H, PMe$_3$), 6.52 (m, 2 H, γ-CH), 6.88 (m, 2 H, β-CH), 7.75 (m, 2 H, Ru-CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz): δ 16.1 (t, J(PC) $=$ 15.3 Hz, PMe$_3$), 19.6 (d, J(PC) $=$ 19.9 Hz, PMe$_3$), 129.4 (s, γ-CH), 138.4 (s, β-CH), 166.6 (dt, J(PC) $=$ 75.5, 16.2 Hz, Ru-CH), 202.5 (q, J(PC) $=$ 12.9 Hz, CO). Anal. Calcd for $C_{26}H_{60}Cl_2O_2P_6Ru_2$: C, 36.16; H, 7.00. Found: C, 36.11; H, 7.10.

[RuCl(CO)(PhPy)(CO)(PPh$_3$)$_2$]$_2$(*μ*-CH$=$CHCH$=$CHCH$=$CH) (8). A mixture of complex **6** (0.5 g, 0.34 mmol) and 4-phenylpyridine (0.21 g, 1.4 mmol) in CH_2Cl_2 (30 mL) was stirred for 30 min. The mixture was then filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (30 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.47 g, 86%. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz): δ 25.2 (s). ^{1}H NMR (CD$_2$Cl$_2$, 300.13 MHz): δ 5.43 (br, 2 H, γ-CH), 6.88 (br, 4 H, C$_5$H$_2$*H*$_2$N), 7.21$-$7.64 (m, 72 H, Ph, β-CH), 7.90 (br, 2 H, Ru-H), 8.55 (br, 4 H, C$_5$*H*$_2$H$_2$N). Anal. Calcd for $C_{102}H_{84}Cl_2N_2O_2P_4Ru_2$: C, 69.34; H, 4.79; N, 1.57. Found: C, 68.63; H, 5.06; N, 2.02.

[RuCl(CO)(PMP)]$_2$(*μ*-CH$=$CHCH$=$CHCH$=$CH) (9). A mixture of complex **6** (0.50 g, 0.34 mmol) and PMP (0.32 g, 0.70 mmol) in CH_2Cl_2 (30 mL) was stirred for 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 5 mL under vacuum. Addition of hexane (30 mL) to the residue produced a pale green-yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.41 g, 89%. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.5 MHz): δ 49.3 (s). ^{1}H NMR (CD$_2$Cl$_2$, 300.13

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(34) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F.; Wonchoba, E. R.; Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 45.

(35) Dahlhoff, W. V.; Nelson, S. M. *J. Chem. Soc. (A)* **1971**, 2184.

MHz): δ 4.24 (dt, J(PH) = 17.1 Hz, J(HH) = 4.8, 4 H, CH*H*(C_5H_3N)CH*H*), 4.63 (dt, J(PH) = 17.1 Hz, J(HH) = 4.8 Hz, 4 H, C*H*H(C_5H_3N)C*H*H), 4.93 (br, 2 H, γ-CH), 5.61 (dt, J(HH) = 15.8 Hz, 3.3 Hz, 2 H, β-CH), 7.15−7.99 (m, 48 H, PPh_2, C_6H_3N, Ru-CH). Anal. Calcd for $C_{70}H_{60}Cl_2N_2O_2P_4Ru_2$: C, 61.90; H, 4.45; N, 2.06. Found: C, 61.72; H, 4.68; N, 2.27.

{[Ru(*t*-BuNC)$_3$(PPh$_3$)$_2$]$_2$(μ-COCH═CHCH═CHCH═CH-CO)}(BPh$_4$)$_2$ (10). To a solution of complex **6** (0.50 g, 0.34 mmol) in CH_2Cl_2 (40 mL) was added *tert*-butyl isocyanide (0.40 mL, 3.5 mmol). The reaction mixture was stirred for 30 min. The solvent was removed completely under vacuum. To the residual was added a solution of $NaBPh_4$ (0.50 g, 1.5 mmol) in methanol (40 mL). The mixture was stirred for 1 h to give an orange-yellow solid, which was collected by filtration, washed with methanol and diethyl ether, and dried under vacuum overnight. Yield: 0.76 g, 89%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ 37.2 (s). ^1H NMR (CD_2Cl_2, 300.13 MHz): δ 1.18 (s, 36 H, *t*-Bu), 1.22 (s, 18 H, *t*-Bu), 5.28 (ddd, J(HH) = 14.7, 7.5, 3.0 Hz, 2 H, γ-CH), 5.56 (dd, J(HH) = 7.5, 3.0 Hz, 2 H, δ-CH), 5.69 (d, J(HH) = 14.7 Hz, 2 H, β-CH), 6.99 (t, J(HH) = 7.2 Hz, 8 H, BPh_4), 7.15 (t, J(HH) = 7.2 Hz, 16 H, BPh_4), 7.45−7.64 (m, 76 H, PPh_3, BPh_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 30.1 (s, *t*-Bu), 30.3 (s, *t*-Bu), 58.5 (s, *t*-Bu), 58.7 (s, *t*-Bu), 122.4 (s, BPh_4), 126.1 (s, δ-CH), 126.3 (s, BPh_4), 129.0 (t, J(PC) = 4.9 Hz, *m*-PPh_3), 131.2 (s, *p*-Ph), 134.6 (t, J(PC) = 4.9 Hz, *o*-Ph), 134.8 (t, J(PC) = 22.3 Hz, ipso-Ph), 136.7 (s, BPh_4), 137.6 (s, γ-CH), 142.2 (s, β-CH), 148.0 (br, Ru−CN), 149.7 (br, Ru-CN), 164.8(q, J(BC) = 49.3 Hz, BPh_4), 260.2 (t, J(PC) = 9.8 Hz, Ru-CO). Anal. Calcd for $C_{158}H_{160}B_2N_6O_2P_4Ru_2$: C, 75.23; H, 6.39; N, 3.33. Found: C, 75.24; H, 6.48; N, 3.39.

RuCl(CH═CHCH═CHC≡CH)(CO)(PMe$_3$)$_3$ (11). To a mixture of tetra-*n*-butylammonium fluoride (5 mL, 1 M in THF) and ethylene glycol (4 mL) was slowly added (*Z*)-Me_3SiC≡CHCH═CHC≡$CSiMe_3$ (**3b**) (1.00 g, 4.54 mmol). The reaction mixture was stirred for 3 h at room temperature to generate (*Z*)-HC≡CHCH═CHC≡CH (**4b**). Most of the THF was removed by rotoary evaporation, and then (*Z*)-HC≡CHCH═CHC≡CH (**4b**) was collected from the reaction mixture by vacuum distillation into a liquid nitrogen cooled flask. The collected **4b** was then diluted with CH_2Cl_2 (15 mL). To the solution of **4b** was added a solution of $RuHCl(CO)(PPh_3)_3$ (1.00 g, 1.05 mmol) in CH_2Cl_2 (80 mL). After the mixture was stirred for 5 min, 10 mL of a THF solution of PMe_3 (1.0 M, 10.0 mmol) was added. The mixture was stirred for 20 h. The volume of the reaction mixture was reduced to 5 mL, and then diethyl ether (20 mL) was added. The solution was filtered through a column of Celite, and the filtrate was concentrated to 5 mL. Addition of hexane (30 mL) to the residue produced a pale yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum overnight. Yield: 0.27 g, 55%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ −20.6 (t, J(PP) = 23.8 Hz), −9.3 (d, J(PP) = 23.8 Hz). ^1H NMR (CD_2Cl_2, 300.13 MHz): δ 1.45 (t, J(PH) = 3.5 Hz, 18 H, PMe_3), 1.52 (d, J(PH) = 6.8 Hz, 9 H, PMe_3), 3.20 (s, 1 H, ≡CH), 4.89 (d, J(HH) = 10.6 Hz, 1 H, δ-CH), 6.48 (t, J(HH) = 10.6 Hz, 1 H, γ-CH), 6.99 (m, 1 H, β-CH), 8.16 (m, 1 H, Ru-CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 16.2 (t, J(PC) = 15.4 Hz, PMe_3), 19.4 (d, J(PC) = 21.2 Hz, PMe_3), 78.9 (s, ≡CH), 82.8 (s, C≡), 94.1 (s, δ-CH), 134.9 (t, J(PC) = 4.5 Hz, γ-CH), 147.0 (dt, J(PC) = 8.8, 2.9 Hz, β-CH), 185.1 (dt, J(PC) = 77.5, 16.3 Hz, Ru−CH), 201.8 (q, J(PC) = 12.8 Hz, CO). Anal. Calcd for $C_{16}H_{32}ClOP_3Ru$: C, 40.90; H, 6.87. Found: C, 40.76; H, 6.91.

(PMe$_3$)$_3$(CO)ClRuCH═CHCH═CHC(═CH$_2$)RuCl(CO)-(PPh$_3$)$_2$ (12). A mixture of complex **11** (0.20 g, 0.43 mmol) and $RuHCl(CO)(PPh_3)_3$ (0.41 g, 0.43 mmol) in CH_2Cl_2 (20 mL) was stirred for 30 min. The volume of the reaction mixture was reduced to ca. 3 mL. Addition of hexane (50 mL) to the residue produced an orange-yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum overnight. Yield: 0.45 g, 90%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ −20.7 (t, J(PP) = 23.1 Hz), −9.0 (d, J(PP) = 23.1 Hz), 30.5 (s). ^1H NMR (CD_2Cl_2, 300.13 MHz): δ 1.27 (t, J(PH) = 3.4 Hz, 18 H, PMe_3), 1.49 (d, J(PH) = 6.8 Hz, 9 H, PMe_3), 5.68 (t, J(HH) = 11.0 Hz, 1 H, CH), 5.96 (d, J(HH) = 11.0 Hz, 1 H, CH), 6.91 (m, 1 H, CH), 7.30−7.76 (m, 33 H, Ru-CH, ═CH_2, PPh_3). Anal. Calcd for $C_{53}H_{63}Cl_2O_2P_5Ru_2$: C, 54.88; H, 5.47. Found: C, 55.02; H, 5.58.

[(PMe$_3$)$_3$(CO)ClRuCH═CHCH═CHC(═CH$_2$)CORu(*t*-BuNC)$_3$(PPh$_3$)$_2$]Cl (13). To a solution of complex **12** (0.2 g, 0.17 mmol) in CH_2Cl_2 (20 mL) was added a solution of *tert*-butyl isocyanide (0.1 mL, 0.88 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 20 min. The volume of the reaction mixture was reduced to ca. 3 mL. Addition of hexane (30 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum overnight. Yield: 0.21 g, 88%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): δ −20.8 (t, J(PP) = 23.1 Hz), −8.6 (d, J(PP) = 23.1 Hz), 34.7 (s). ^1H NMR (CD_2Cl_2, 300.13 MHz): δ 0.99 (s, 9 H, *t*-Bu), 1.10 (s, 18 H, *t*-Bu), 1.41 (t, J(PH) = 3.4 Hz, 18 H, PMe_3), 1.57 (d, J(PH) = 6.8 Hz, 9 H, PMe_3), 4.90 (s, 1 H, ═CH_2), 5.06 (d, J(HH) = 11.8 Hz, 1 H, δ-CH), 5.30 (s, 1 H, ═CH_2), 5.90 (t, J(HH) = 11.8 Hz, 1 H, γ-CH), 6.67 (m, 1 H, β-CH), 7.39−7.68 (m, 30 H, PPh_3), 7.85 (m, 1 H, RuCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 17.15 (t, J(PC) = 15.3 Hz, PMe_3), 20.39 (d, J(PC) = 21.1 Hz, PMe_3), 29.91 (s, *t*-Bu), 30.05 (s, *t*-Bu), 58.34 (s, *t*-Bu), 58.44 (s, *t*-Bu), 115.4 (s, δ-CH), 118.7 (s, CH_2), 128.8 (t, J(PC) = 4.6 Hz, *m*-Ph), 130.9 (s, *p*-Ph), 133.4 (s, β-CH), 134.6 (t, J(PC) = 5.5 Hz, *o*-Ph), 135.3 (t, J(PC) = 22.1 Hz, *ipso*-Ph), 137.9 (s, γ-CH), 146.5 (br, Ru-CN), 147.2 (s, *C*-CO), 148.5 (br, Ru-CN), 178.7 (dt, J (PC) = 78.1, 16.5 Hz, Ru-CH), 202.6 (q, J(PC) = 11.6 Hz, CO), 257.2 (t, J(PC) = 9.2 Hz, CO). Anal. Calcd for $C_{68}H_{90}Cl_2N_3O_2P_5Ru_2 \cdot 2CH_2Cl_2$: C, 53.24; H, 6.00; N, 2.66. Found: C, 53.22; H, 6.41; N, 2.83.

Crystallographic Analysis for 10. The orange-red single crystals of **10** were grown by layering of diethyl ether on top of a CH_2Cl_2 solution of complex **10**. During the process, dichromethane cocrystallized with **10**. A yellow single crystal with approximate dimensions of 0.25 × 0.20 × 0.12 mm was mounted in a glass capillary for diffraction experiment. Intensity data were collected on a Bruker SMART CCD area detector and corrected for SADABS (Siemens Area Detector Absorption)[36] (from 0.8265 to 1.0000 on *I*). The structure was solved by Patterson methods, expanded by difference Fourier syntheses, and refined by full matrix least-squares on F^2 using the Bruker SHELXTL (Version 5.10)[37] program package. The molecule is centro-symmetric with the inversion center at the midpoint of C4 and C4A; thus the crystallographic asymmetric unit contains half of one molecule and three CH_2Cl_2 solvent molecules in general positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogens were introduced at their geometric positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table 1, and selected bond distances and angles are given in Table 2.

Acknowledgment. The authors acknowledge financial support from the Hong Kong Research Grants Council.

Supporting Information Available: Tables of bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for {[Ru(*t*-BuNC)$_3$(PPh$_3$)$_2$]$_2$(μ-COCH═CHCH═CHCH═CHCO)}(BPh$_4$)$_2 \cdot$6CH$_2$Cl$_2$. The materials are available free of charge via the Internet at http://pubs.acs.org.

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[36] Sheldrick, G. M. *SADABS*, Empiracal Absorption Correction Program; University of Göttingen: Germany, 1996.

[37] Bruker. *SHELXTL Reference Manual (Version 5.1)*; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997.