Synthesis of New Ruthenium(II) Carbonyl Hydrido, Alkenyl, and Alkynyl Complexes with Chelating Diphosphines

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Substitution of one or two triphenylphosphine ligands of $Ru(CO)ClH(PPh_3)_3$ by bidentate diphosphines $Ph_2P(CH_2)_nPPh_2$ (L-L) (n = 1, dppm; n = 2, dppe; n = 3, dppp; n = 4, dppb) or 1,1′-bis(diphenylphosphino)ferrocene (dppf) led to hydrides $Ru(CO)ClH(PPh_3)_2$(L-L) or Ru(CO)ClH(PPh_3)(L-L). The hydrido complexes were characterized spectroscopically and by one X-ray structure. Hydride Ru(CO)ClH(PPh_3)(dppf) crystallizes in the monoclinic space group $P2_1/n$, with a = 17.768(1) Å, b = 25.252(2) Å, c = 11.213(1) Å, β = 92.83(1)°, Z = 4, and V = 4459.3(6) Å^3. Reaction of $Ru(CO)ClH(PPh_3)_3$ or $[Ru(CO)H(MeCN)_2(PPh_3)_2]^+PF_6^-$ with 2 equiv of diphosphines L-L led to $[Ru(CO)H(L\text{-}L)_2]^+A^-$ (L-L = dppm, dppe, dppp) (A = Cl, PF_6). Hydrides $Ru(CO)ClH(PPh_3)_2$(L-L) react with 1-alkynes to give alkenyl complexes Ru(CO)Cl(CH=CHR)(PPh_3)(L-L) with a chelating diphosphine ligand. $Ru(CO)ClH(PPh_3)$-(L-L) gave σ-alkynyl complexes Ru(CO)Cl(C≡CR)L(L-L) directly in their reactions with 1-alkynes. The hydride with dppb as the ligand showed the highest reactivity. The preparation of hexacoordinated alkenyl derivatives Ru(CO)Cl(CH=CHR)(PPh_3)(L-L) with a chelating diphosphine was carried out by treatment of other alkenyl derivatives with the diphosphines. Surprisingly, reaction of alkenyls $Ru(CO)Cl(CH{=}CHR)(Me_2Hpz)(PPh_3)_2$ (R = CMe_3, p-MeC_6H_4) with dppf led to complexes Ru(CO)Cl(CH=CHR)(Me_2Hpz)(dppf) by substitution of both PPh_3 ligands instead of the dimethylpyrazole. Ruthenium alkenyls Ru-(CO)Cl(CH=CHR)L(dppf) (L = Me_2Hpz, PPh_3) react cleanly with 1-alkynes at room temperature to give alkynyl complexes Ru(CO)Cl(C≡CR)L(dppf) in good yield. This reaction was applied to the synthesis of a bimetallic complex Ru(CO)Cl(PPh_3)(dppf)(C≡C-p-C_6H_4C≡C)-Ru(CO)Cl(PPh)(dppf) as a mixture of meso and *dl* diastereomers.

Introduction

The hydroruthenation of alkynes has been usually carried out with hexacoordinated ruthenium(II) hydrides containing monophosphine ligands.[2,3] Less attention has been given to the employment of di- or triphosphines as the ligands.[4] We have recently reported that small modifications on the ligands for Ru(II) led to the direct formation of (σ-alkynyl)-[5] or (σ-butenynyl)ruthenium complexes in the reaction between ruthenium hydrides and alkynes.[6,7] In this processes, labile alkenyl complexes were formed first, which react with further molecules of alkyne to give the observed products.[5-7] Alternatively, butadienyl complexes can also be formed by insertion of the second alkyne into the Ru–C bond of the (σ-alkenyl)ruthenium complex.[2b,4b,8] Some ruthenium hydride complexes are

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active catalysts for the hydrocarbonylation,[9] hydrogenation, and hydrosilylation of alkynes.[10] However, despite the synthetic potential of the hydroruthenation reaction for the formation of carbon–carbon bonds, few catalytic processes have been developed on the basis of this chemistry.[7a,11]

In order to increase the reactivity of the intermediates formed in the reactions of ruthenium hydrides with alkynes, we decided to explore the reactivity of a series of ruthenium hydrido and alkenyl complexes with chelating diphosphine ligands with different bite angles.[12] Our goal was the development of a general synthesis of ruthenium alkynyl complexes by substitution of the alkenyl group of isolable ruthenium derivatives. In this paper we describe the synthesis of ruthenium carbonyl hydrides with the diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 3, dppp; n = 4, dppb), and 1,1′-bis(diphenylphosphino)ferrocene (dppf) and their reactivity toward 1-alkynes leading to the formation of σ-alkenyl or σ-alkynyl complexes. Some ruthenium carbonyl hydrides with the ligands dppm and dppe have been described, but their reactions with alkynes were not studied.[9,13–15] Alternative routes for the synthesis of these σ-alkenyl or σ-alkynyl derivatives are also reported. Interestingly, coordination of dppf facilitated the cleavage of the σ-alkenyl ligand by the 1-alkyne leading to the formation of σ-alkynyl complexes under mild conditions.

Results and Discussion

Synthesis of Ruthenium Hydrides with Diphosphine Ligands. The readily available complex Ru(CO)ClH(PPh_3)$_3$ (**1**)[16] reacts with 1 mol equiv of diphosphines dppm, dppe, dppp, and dppb to yield three different types of hydrides (**I**–**III**), depending on the reaction time and the temperature (Scheme 1). The reaction of **1** with dppm at room temperature for 30 min in CH_2Cl_2 or 1:1 CH_2Cl_2–EtOH gives hydride **2**, containing a monodentate diphosphine ligand. When the reaction was performed for longer reaction times, a mixture of isomeric hydrides **5** and **9** was obtained, leading to **9** as the major product. Similarly, dppe and dppp gave first the substitution products **3** and **4**, and after longer reaction times or more vigorous conditions, complexes **6** and **7** were formed. Complex **6** has been prepared before from **1** in high yield.[14] When the reaction of hydride **1** with dppe was allowed to proceed for longer times, small amounts of another hydride formed, which was characterized tentatively as **10**. In the case of dppb ligand, the reaction led to the formation of hydride **8** as the major product. With dppp and dppb no hydride of type **III** was observed. Ruthenium complexes of type **I** showed their hydride resonance around −7 ppm in the ^{1}H NMR spectra with the expected couplings to the *trans* and *cis* phosphine ligands. Complex **2**, with a dppm ligand *trans* to the hydride, also showed a ^3J of 3.9 Hz with the distant phosphorous of the *trans* diphosphine. The hydride resonance of complexes **II** appeared between −5.89 and −8.13 ppm coupled to the *trans* and the *cis* phosphine ligands. Hydrides **III** showed resonances shifted to higher fields (−13.5 to −15.4 ppm) with three different *cis* couplings to phosphine ligands. Although the alternative stereochemistry cannot rigorously be excluded, the structure shown, with the hydride *trans* to the chloride, is favored on the basis of the chemical shift displayed by the hydride, similar to those of related hydrides Ru(CO)ClHL(PPh_3)$_2$.[2e,6] Hydrides **I** and **II** displayed a CO stretch in the IR around 1920 cm^{-1}, while hydrides **III** showed absortions at higher frequencies (1960 cm^{-1}).

When the reactions were carried out with 2 equiv of diphosphine, the complexes **IV** were isolated (Scheme 1). These ruthenium complexes contain two bidentate diphosphine ligands in the equatorial plane. Alternatively, this type of complex could be prepared, as the hexafluorophosphate salt (**11b**, **12b**), by reaction of the cationic hydride complex [Ru(CO)H(MeCN)$_2$(PPh_3)$_2$]PF_6 (**14a**)[2c] with 2 equiv of the corresponding diphosphine. Complexes **11** and **12** have been prepared before as the hexafluoroantimonate or tetraethyl borate salts by decarbonylation of formylruthenium complexes.[13] The diphosphine dppb, with the highest bite angle, failed to form a hydride complex of type **IV** from either **1** or **14a**. The ruthenium hydride complexes **11**–**13** showed CO absortions around 1990–1980 cm^{-1}, almost 70 cm^{-1} greater than observed for complexes of type **I** and **II**. The appearance of a single ^{31}P resonance and a quintet in the ^{1}H NMR spectra for the hydride ligand of hydrides **IV** allows for the unequivocal assignment of their structures.

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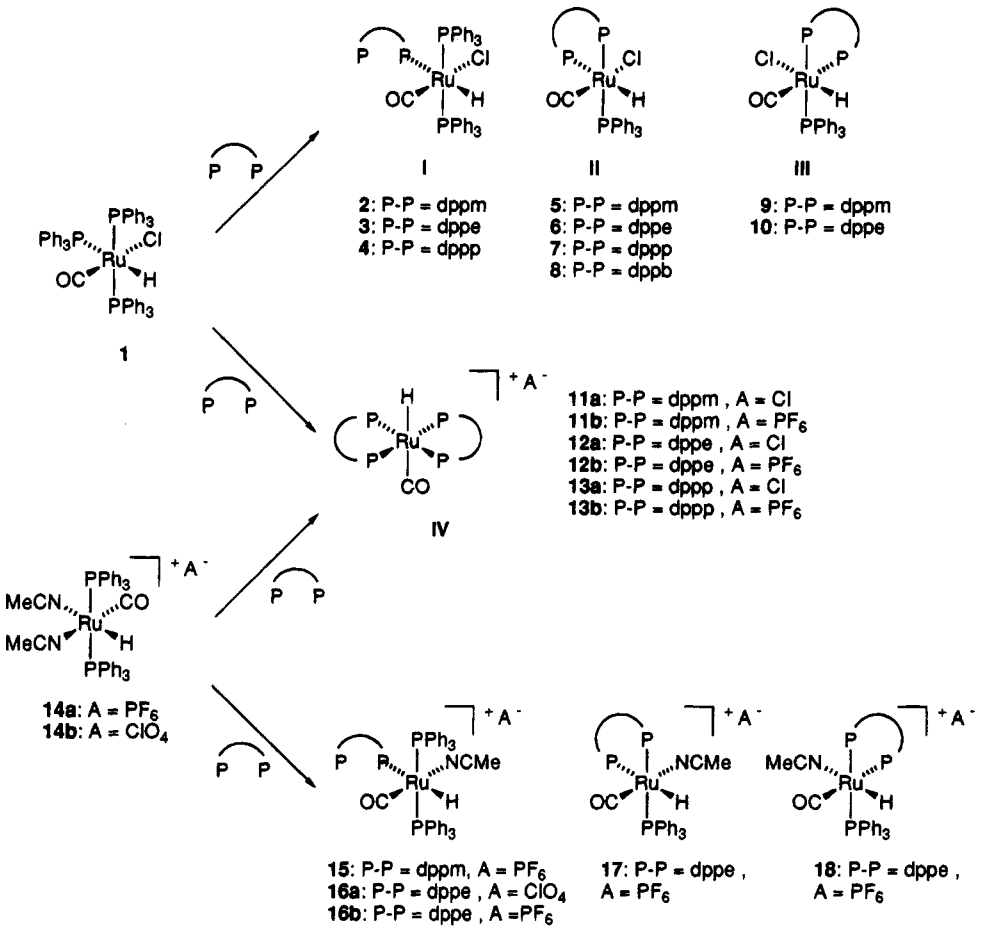
Scheme 1



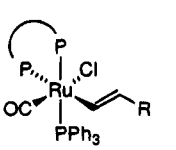
Reactions of cationic hydrides **14**[17] with dppm and dppe in a 1:1 molar ratio at room temperature and for short reaction times gave rise to hydrides **15** and **16**, by selective substitution of one nitrile by a monodentate diphosphine ligand. The tetrafluoroborate salt of the cation of **16** has been previously prepared by the same procedure.[9] Longer reaction times led to the formation of isomers **17** and **18** in a 2:1 ratio (Scheme 1).

Reaction of starting hydride **1** with dppf gave **19**, which showed in the ^1H NMR spectrum a ddd at −7.93 ppm with $^2J(^1H-^{31}P)$ of 108.8, 27.7, and 21.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum showed an ABX spin system with $^2J(^{31}P-^{31}P)$ of 305.8, 17.7, and 12.9 Hz. These data are in agreement with the structure shown in Scheme 2. This assignment was confirmed by an X-ray determination (Figure 1). Selected bond distances and angles are given in Table 1. The cyclopentadienyl groups are staggered (20.7(9)°) and almost parallel (dihedral angle of 3.1(5)° between the least-squares planes) and do not deviate significantly from planarity. The angle between the apical phosphorous atoms and Ru [P(2)−Ru−P(3)] of 154.0(1)° deviates significantly from the ideal octahedral coordination toward the hydride ligand.

Hydride **19** could also be prepared from hydrides **20**[3e] and **21**,[2e] by ligand substitution with dppf in toluene under reflux conditions. Treatment of cationic hydride **22**[5] with dppf afforded cationic complex **23** with a pyridine ligand. In an analogous fashion, the related acetonitrile complex **24** was obtained from **19** by reaction with NH_4PF_6 in acetonitrile under reflux conditions (Scheme 2). These complexes have spectroscopic data fully consistent with the assigned structures. All attempts to synthesize a ruthenium hydride with two dppf ligands failed. Presumably, because of the large bite angle of dppb and dppf, complexation of two of these chelating diphosphines in the equatorial plane is precluded by steric hindrance of the phosphine phenyl groups.

Reactions with Alkynes. The formation of these unsaturated intermediates is a necessary condition in the hydroruthenation reaction. In principle, with the exception of complexes **IV**, all other hydrides can suffer facile elimination of a phosphine ligand under mild conditions to give a reactive five-coordinated hydride.

However, only the ruthenium hydrides of the type **I** react smoothly with 1-alkynes to give alkenyl complex **25**−**29**. After the addition of the alkyne, an intense red



25: P-P = dppm , R = *t*-Bu
26: P-P = dppm , R = Ph
27: P-P = dppe , R = *t*-Bu
28: P-P = dppe , R = *p*-MeC_6H_4
29: P-P = dppp , R = *p*-MeC_6H_4

solution was observed, characteristic of the coordinatively unsaturated alkenyl complexes Ru(CO)Cl(CH=

(17) Hydride **14**: Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60.

Scheme 2

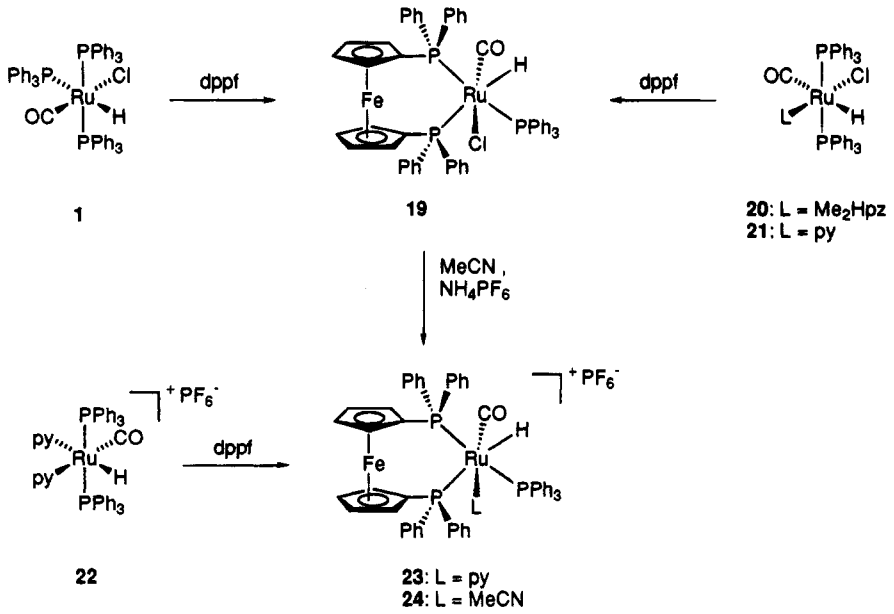


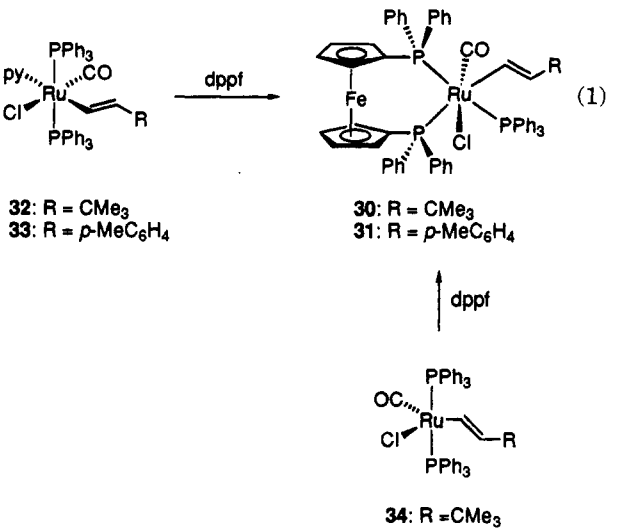
Table 1. Selected Bond Distances (Å)[a] and Bond Angles (deg) for Hydride 19[b]

Ru—Cl	2.476(3)	Fe—C(12)	2.05(1)
Ru—P(1)	2.518(4)	Fe—C(13)	2.04(1)
Ru—P(2)	2.392(4)	Fe—C(14)	2.03(1)
Ru—P(3)	2.369(3)	P(1)—C(20)	1.81(1)
Ru—C(1)	1.83(2)	Fe—C(20)	2.03(1)
Ru—H(1)	1.62	Fe—C(21)	2.04(1)
C(1)—O(1)	1.10(2)	Fe—C(22)	2.05(1)
P(2)—C(10)	1.80(1)	Fe—C(23)	2.05(1)
Fe—C(10)	2.01(1)	Fe—C(24)	2.04(1)
Fe—C(11)	2.02(1)		
Cl—Ru—P(1)	96.0(1)	P(1)—Ru—H(1)	170.7
Cl—Ru—P(2)	83.1(1)	P(2)—Ru—P(3)	154.0(1)
Cl—Ru—P(3)	88.3(1)	P(2)—Ru—C(1)	98.3(6)
Cl—Ru—C(1)	177.6(5)	P(2)—Ru—H(1)	76.5
Cl—Ru—H(1)	92.9	P(3)—Ru—C(1)	89.6(6)
P(1)—Ru—P(2)	102.2(1)	P(3)—Ru—H(1)	79.5
P(1)—Ru—P(3)	103.1(1)	C(1)—Ru—H(1)	85.6
P(1)—Ru—C(1)	85.5(5)	Ru—C(1)—O(1)	179(1)

[a] Mean (C—C) in Cp rings = 1.42(2); mean (C—C) in Ph rings = 1.37(2); mean (P—C) in P—Ph = 1.84(1) Å. [b] Mean C—C—C in Cp rings = 108(1)°; mean C—C—C in Ph rings = 120(2)°.

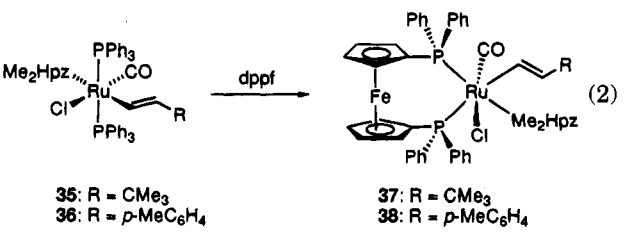
$CHR)(PPh_3)_2$.[2a,b,8a] Subsequent slow reaction of these complexes with the bidentate ligand provided the white alkenyl complexes formally derived from hydrides of the type **II**. The direct reaction of hydrides **II** with alkynes failed to give any alkenyl complex. Alkenylruthenium derivatives **25**–**29** present IR and NMR spectra fully consistent with the proposed structures. Alternatively, alkenyls **25**–**29** could be prepared in a one-pot process by reaction of hydride **1** with the alkyne and subsequent addition of the appropriate diphosphine. Thus, complexes of type **I** behave as a surrogate of hydride **1**, leading to the formation of the same coordinatively unsaturated hydride $Ru(CO)ClH(PPh_3)_2$, which, after insertion of the alkyne, reacts with the diphosphine to give the hexacoordinated alkenyl complexes.

Hydrides of type **II** or **III** failed to give any alkenyl complex under all the reaction conditions examined. Similarly, complexes **19**, **23**, and **24** with a chelating dppf did not afford the expected alkenyl complexes. However, complexes **30** and **31** were prepared by substitution of the pyridine and triphenylphosphine ligands of alkenyl complexes **32** and **33**[2e] with dppf in toluene under reflux conditions (eq 1). The ^1H NMR



spectrum of **30** showed the α-alkenyl hydrogen at 6.34 ppm as a ddt coupled to the alkenyl β-hydrogen and a *trans* and two *cis* phosphorus nuclei, respectively. Its $^{31}P\{^1H\}$ NMR spectrum displayed three dd at 22.96, 18.36, and −5.40 ppm, consistent with the assigned structure. Alkenyl complex **30** could also be prepared by treatment of the coordinatively unsaturated complex $Ru(CO)Cl(CH{=}CHCMe_3)(PPh_3)_2$ (**34**)[2a,b,8a] with dppf.

Surprisingly, alkenyl complexes **35** and **36**,[3f] with a dimethylpyrazole ligand *trans* to the alkenyl, reacted with dppf in toluene under reflux conditions to afford complexes **37** and **38** (eq 2), which retained the hetero-



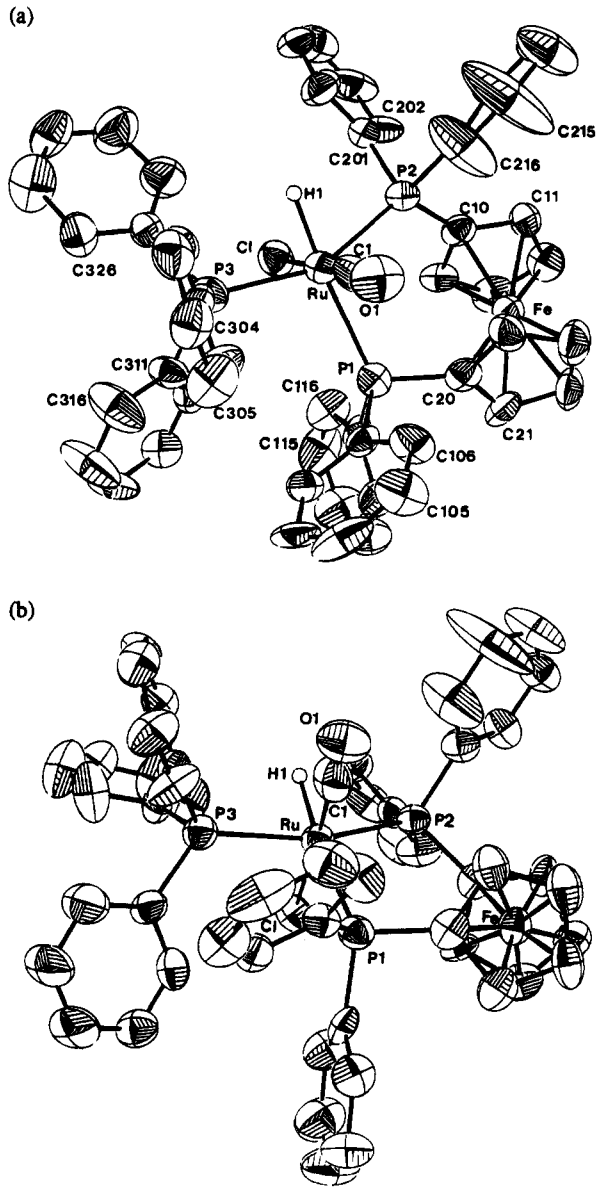
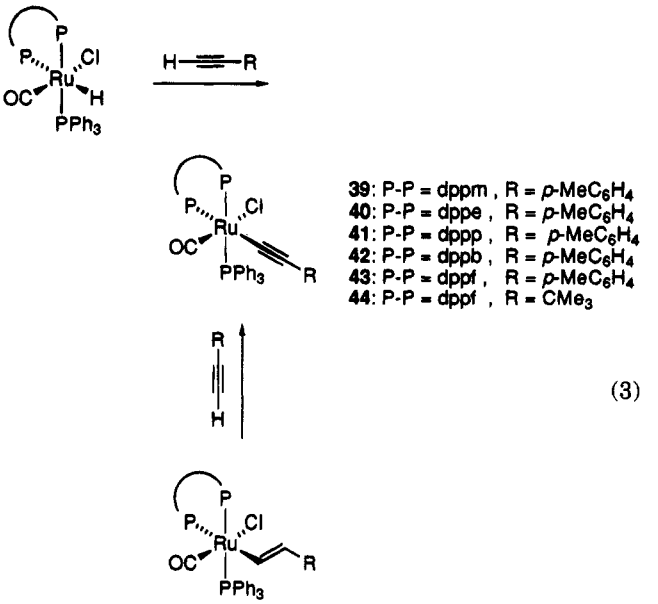


Figure 1. Two views (ORTEP drawing) of hydrido complex Ru(CO)HCl(PPh_3)(dppf) (**19**) (thermal ellipsoids at the 50% level). The PPh_3 and dppf hydrogen atoms are omitted for clarity.

cyclic ligand instead of the triphenylphosphine. This result is in sharp contrast with the usual reactivity displayed by these types of octahedral ruthenium complexes in substitution reactions. The analogous reactions of **35** and **36** with diphosphines $PPh_2(CH_2)_nPPh_2$ (n = 1–4) were not observed. As shown before, complexes **32** and **33** substituted the pyridine ligand in the reaction with dppf.[18] The arrangement of ligands around ruthenium of derivatives **37** and **38** was assigned tentatively on the basis of their spectroscopic characteristic and by comparison with the structures of **31**. Alkenyl **37** showed in the ^1H NMR spectrum the α-alkenyl hydrogen at 6.55 ppm as a ddd coupled to the alkenyl β-hydrogen and *trans* and *cis* phosphorus nuclei. The $^{13}C\{^1H\}$ NMR spectrum of **38** showed the carbonyl resonance at 205.00 ppm as a dd, coupled to a different *cis* phosphorus. The $^{31}P\{^1H\}$ NMR spectrum showed the expected AB system with a coupling of 12–13 Hz, characteristic of *cis* phosphine ligands. These data are consistent with the assigned structures, although the alternative formulation with the heterocyclic ligand *trans* to the carbonyl and the chloride *trans* to a phosphine cannot be excluded.

As anticipated, hydrides **IV** showed no proclivity to react with 1-alkynes due to their reluctance to undergo substitution reactions.

Alkynyl Complexes. In contrast with the behavior observed for hydrides **I**, the reaction of hydrides of type **II** (Scheme 1) with 1-alkynes led directly to the formation of alkynyl complexes (eq 3). Alternatively, these

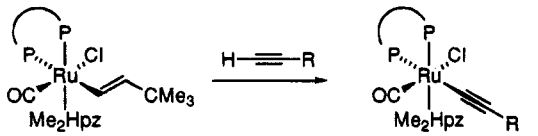


complexes could be prepared starting from alkenyl complexes by reaction with the excess 1-alkyne. Usually these reactions proceed slowly in 1,2-dichloroethane at 80 °C for several hours and require the addition of excess alkyne. The alkynyl group of these complexes is that derived from the added 1-alkyne.[5] The formation of the corresponding 1-alkene was confirmed when the reactions were performed in sealed NMR tubes.[5,6] Additionally, partial oligomerization of the alkynes was also observed in a few cases. Hydride **8**, with a dppb ligand, was more reactive than **5**–**7**, leading to alkynyl **42** at room temperature. The alkynyl complexes exhibit ν(C≡C) in the IR at 2100 cm^{-1} as the most significant spectroscopic feature. Their ν(CO) appeared in the range 1960–1980 cm^{-1}.

Hydride **19**, with a dppf ligand, reacted with excess *p*-tolylacetylene in ethanol under reflux conditions to give **43** (eq 3). However, the same complex **43** could be more conveniently prepared by treatment of alkenyl complex **30** with excess *p*-tolylacetylene. Remarkably, this reaction proceeds smoothly in dichloromethane at room temperature.[19] Similarly, reaction of **30** with excess *tert*-butylacetylene gave **44**. The stereostructure around the metal of these alkynyl complexes was assigned tentatively by analogy with those of the alkenyl complexes. Alkenyl complex **37**, with dppf and dimethylpyrazole ligands, also reacted at room temperature with excess alkyne to give the alkynyl complex **45** (eq 4).

(18) Pyridine and pyrazole coordinate to Ru(II) with similar strength: Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(19) For a recent synthesis of acetylide complexes of Ru containing dppf as the ligand *via* vinylidene complexes, see: Sato, M.; Sikino, M. *J. Organomet. Chem.* **1993**, *444*, 185.

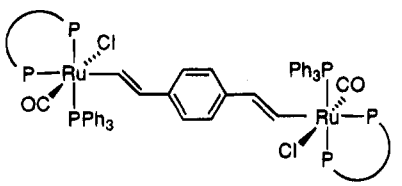


(4)

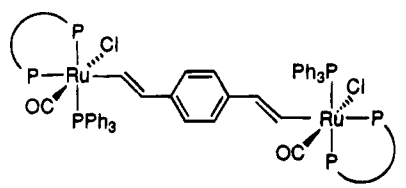
37: P-P = dppf

45: P-P = dppf, R = *p*-MeC$_6$H$_4$

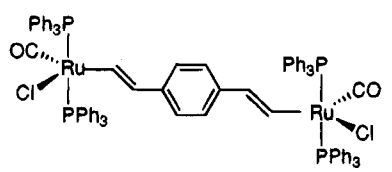
The synthesis of bimetallic complexes in which the metal atoms are connected by an organic group has received great attention in recent years.[20-22] We decided to attempt the preparation of simple diruthenium complexes by reaction of ruthenium hydrides or alkenyls with a dialkyne. The bimetallic complexes **46** with the metals separated by a *p*-diethenylbenzene spacer were prepared in good yield directly by addition of dppf to a mixture of hydride **1** and *p*-diethynylbenzene. The ^{31}P-{^{1}H} NMR spectrum of **46** showed two ABX spin systems corresponding to a 1:1 mixture of meso (**46a**)- and *dl* (**46b**) diastereomers. The same mixture of



46a: P-P = dppf

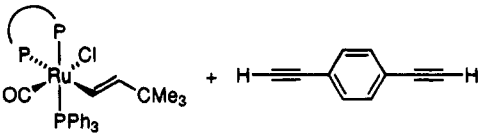


46b: P-P = dppf

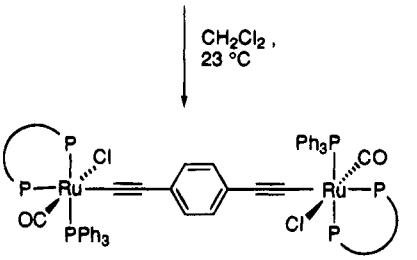


47

complexes was obtained by reaction of dppf with complex **47**, the product of hydroruthenation of *p*-diethenylbenzene with hydride **1**. More interestingly, the facile replacement of alkenyl by alkynyl ligands observed for the alkenylruthenium complexes with dppf (eq 3) was employed for the synthesis of bimetallic complexes **48** as shown in eq 5. Alkenyl **30** (2 equiv)



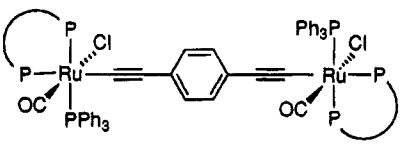
30: P-P = dppf



(5)

48a: P-P = dppf

+



48b: P-P = dppf

reacted smoothly with 1 equiv of *p*-diethynylbenzene in CH_2Cl_2 at room temperature, leading to the formation of **48**, isolated 77% yield as a 1:1 mixture of meso and *dl* diastereomers. Current methods for the synthesis of bimetallic complexes connected through ethynyl bridges are based on substitution or transmetalation with acetylides.[23] The reaction shown in eq 5 opens a new route to this class of bimetallic compounds.

Summary

Substitution of two triphenylphosphine ligands of Ru(CO)ClH(PPh$_3$)$_3$ (**1**) by bidentate diphosphines led to hydrides which gave only σ-alkynyl complexes in their reaction with 1-alkynes. The highest reactivity was observed with hydride **8** with dppb as the ligand. It is interesting that **1**, and related hydrides, led smoothly to alkenylruthenium complexes[2] or butenynyl derivatives under more forcing conditions.[6] The preparation of hexacoordinated alkenyl derivatives with a chelating diphosphine was achieved indirectly by ligand substitution from other alkenyl derivatives. Surprisingly, reaction of alkenyls **35** and **36** with dppf led to complexes **37** and **38** by substitution of both PPh$_3$ ligands instead of the dimethylpyrazole. Ruthenium alkenyls **30** or **37** with a dppf ligand react cleanly with 1-alkynes at room temperature to give alkynyl complexes in good yield. This reaction was applied to the synthesis of bimetallic complexes **48**, isolated as a mixture of meso and *dl* diastereomers.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker AM 200 (200 MHz) or a Varian XL-300 (300 MHz) spectrometer in $CDCl_3$.

(20) (a) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339. (b) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (c) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171.

(21) (a) Wang, S.; Fackler, J. P. *Organometallics* **1990**, *9*, 111. (b) Antonelli, D. M.; Cowie, M. *Organometallics* **1990**, *9*, 1818. (c) Bruno, G.; Lo Schiavo, S.; Rotondo, E.; Arena, C. G.; Faraone, F. *Organometallics* **1989**, *8*, 886. (d) MacKenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8.

(22) (a) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerhan, M. P.; Porter, P. L.; Charchard, E. A.; Lee, G. H. *Polymer* **1987**, *28*, 553. (b) Fyfe, H. B.; Mlekuz, D.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188. (c) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1991**, 187.

(23) See, for example: (a) Zhos, Y.; Seyler, J. W.; Wang, W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509. (b) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1990**, *114*, 4411. (c) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466. (d) Kousantonis, G. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 2361. (e) Lo Sterzo, C. *Organometallics* **1990**, *9*, 3185.

Some second-order couplings are treated as pseudo-first-order systems (pd, pseudo doublet; pt, pseudo triplet). $^{13}C\{^1H\}$NMR spectra were recorded on a Bruker AM 200 (50 MHz) in $CDCl_3$. Only significant resonances are given. $^{31}P\{^1H\}$NMR spectra were recorded on a Varian XL-300 or a Bruker AM 300 (121 MHz) with H_3PO_4 as the external standard. All $^{31}P\{^1H\}$NMR second-order spectra, except those for **23** and **43**, were calculated with the program PANIC of Bruker. IR spectra were recorded on a Pye-Unicam SP-3-300S spectrometer using KBr disks. Elemental analyses were performed at the Instituto de Química Orgánica (CSIC). Dichloromethane and 1,2-dichloroethane were freshly distilled from calcium hydride. All reactions were carried out under a N_2 or Ar atmosphere. All alkenyl complexes described in this paper have the *E* stereochemistry.

Hydrides **1**,[13a] **14a**,[2c] **14b**,[17] **20**,[3e] **21**,[2e] and **22**[5] were prepared according to known procedures. *p*-Diethynylbenzene was prepared from 1-bromo-4-iodobenzene and (trimethylsilyl)-acetylene by a small modification of a known method.[24]

Synthesis of Ru(CO)ClH(PPh$_3$)$_2$(dppm) (2). To a solution of **1** (92 mg, 0.10 mmol) in 1:1 CH_2Cl_2–EtOH (10 mL) was added dppm (75 mg, 0.19 mmol). The mixture was stirred at 23 °C for 30 min. After the mixture was cooled to −15 °C, a crystalline precipitate appeared which was filtered off and washed with Et_2O to yield **2** (74 mg, 71%) as a white amorphous powder: IR (cm^{-1}) ν(C≡O) 1918 vs; ^1H NMR (300 MHz) δ 6.80–7.55 (m, 46 H), 6.53 (t, J = 7.0 Hz, 4 H), 2.54 (s, 2 H), −7.34 (dtd, J = 107.6, 23.5, 3.9 Hz, 1 H); $^{31}P\{^1H\}$NMR δ 39.14 (d, J = 16.1 Hz, 2 P), 4.46 (m, 1 P), −24.26 (d, J = 12.1 Hz, 1 P). Anal. Calcd for $C_{62}H_{53}ClOP_4Ru$: C, 69.30; H, 4.97. Found: C, 68.73; H, 5.00.

Synthesis of Ru(CO)ClH(PPh$_3$)$_2$(dppe) (3). To a solution of **1** (147 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) was added dppe (62 mg, 0.15 mmol). The mixture was stirred at 23 °C for 20 min. The mixture was concentrated, and Et_2O was added to give a greenish white precipitate. This mixture was stirred for 10 min and filtered to yield crude **3** (80 mg, crude yield 47%) as a greenish white solid after washing with ethyl ether and hexane. Hydride **3** was contaminated with small amounts of hydrides **6** and **10**, and a correct microanalysis was not obtained: IR (cm^{-1}) ν(C≡O) 1920 vs; ^1H NMR (200 MHz) δ 7.80–6.65 (m, 50 H), 2.08–0.88 (m, 4 H), −7.62 (dt, J = 100.0, 25.0 Hz, 1 H). Hydride **10** could be detected by ^1H NMR (200 MHz) at δ (only significant signal) −15.43 (ddd, J = 33.0, 20.0, 17.0 Hz, 1 H).

Synthesis of Ru(CO)ClH(PPh$_3$)$_2$(dppp) (4). To a solution of **1** (224 mg, 0.23 mmol) in CH_2Cl_2 (15 mL) was added dppp (97 mg, 0.23 mmol). The mixture was stirred at 23 °C for 20 min. The solvent was evaporated, and the residue was triturated with Et_2O to yield **4** (225 mg, 87%) as a white grayish solid: IR (cm^{-1}) ν(C≡O) 1920 vs; ^1H NMR (200 MHz) δ 7.80–6.75 (m, 50 H), 1.75–1.40 (m, 3 H), 1.35 (m, 1 H), 0.95 (m, 1 H), 0.70 (m, 1 H), −7.04 (dt, J = 104.1, 24.2 Hz, 1 H). Anal. Calcd for $C_{64}H_{57}ClOP_4Ru$: C, 69.72; H, 5.21. Found: C, 69.85; H, 5.18.

Synthesis of Ru(CO)ClH(PPh$_3$)(dppm) (5, 9). To a solution of **1** (92 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added dppm (75 mg, 0.19 mmol). The mixture was stirred at 23 °C for 72 h. After being cooled to −15 °C, a crystalline precipitate appeared which was filtered off and washed with Et_2O to yield a mixture of isomeric hydrides **5** and **9** (74 mg, 70%), which could not be separated. **5**: IR (cm^{-1}) ν(C≡O) 1920 vs; ^1H NMR (200 MHz) δ 8.00–6.90 (m, 35 H), 4.22–4.31 (m, 2 H), −8.13 (ddd, J = 128.4, 19.1, 13.3 Hz, 1 H). **9**: IR (cm^{-1}) ν(C≡O) 1960 vs; ^1H NMR δ 8.00–6.90 (m, 35 H), 4.54–4.65 (m, 2 H), −13.59 (ddd, J = 22.6, 19.6, 16.8 Hz, 1 H).

Synthesis of Ru(CO)ClH(PPh$_3$)(dppe) (6). To a solution of **1** (244 mg, 0.26 mmol) in CH_2Cl_2 (16 mL) was added dppe (102 mg, 0.26 mmol). The mixture was stirred at 23 °C for 24 h. The resulting suspension was filtered, and the solvent was evaporated. The residue was triturated with Et_2O to yield **6** (175 mg, 82%) as a pale gray solid after washing with hexane: IR (cm^{-1}) ν(C≡O) 1925 vs; ^1H NMR (200 MHz) δ 8.02–7.95 (m, 2 H), 7.71–7.64 (m, 2 H), 7.54–6.97 (m, 31 H), 2.87–2.72 (m, 2 H), 2.50–2.40 (m, 2 H), −5.89 (ddd, J = 115.2, 20.2, 16.8 Hz, 1 H). Anal. Calcd for $C_{45}H_{40}ClOP_3Ru$: C, 65.42; H, 4.88. Found: C, 65.14; H, 4.76.

Synthesis of Ru(CO)ClH(PPh$_3$)(dppp) (7). To a solution of **1** (311 mg, 0.33 mmol) in CH_2Cl_2 (22 mL) was added dppp (135 mg, 0.33 mmol). The mixture was heated under reflux conditions for 5.5 h. The solvent was evaporated, and the residue was triturated with Et_2O to yield **7** (216 mg, 79%) as a yellowish solid: IR (cm^{-1}) ν(C≡O) 1920 vs; ^1H NMR (200 MHz) δ 8.03–7.96 (m, 2 H), 7.47–6.80 (m, 33 H), 3.38–3.29 (m, 1 H), 3.04–2.87 (m, 1 H), 2.40–2.34 (m, 1 H), 2.20–2.05 (m, 2 H), 1.80–1.76 (m, 1 H), −6.28 (ddd, J = 108.2, 22.9, 17.0 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 41.80 (dd, J = 275.6, 21.8 Hz, 1 P), 27.40 (dd, J = 275.6, 24.5 Hz, 1 P), 6.01 (dd, J = 27.1, 21.8 Hz, 1 P). Anal. Calcd for $C_{46}H_{42}ClOP_3Ru$: C, 65.98; H, 5.04. Found: C, 65.75; H, 4.97.

Synthesis of Ru(CO)ClH(PPh$_3$)(dppb) (8). To a solution of **1** (100 mg, 0.11 mmol) in CH_2Cl_2 (10 mL) was added dppb (47 mg, 0.11 mmol). The mixture was stirred at 23 °C for 7.5 days. The solvent was evaporated, and the residue was triturated with Et_2O to yield **8** (216 mg, 81%) as a pale beige solid: IR (cm^{-1}) ν(C≡O) 1920 vs; ^1H NMR (200 MHz) δ 7.95–7.62 (m, 2 H), 7.48–7.07 (m, 33 H), 2.94–2.88 (m, 1 H), 2.54–2.39 (m, 3 H) 1.70–1.50 (m, 4 H), −7.05 (dt, J = 108.4, 22.2 Hz, 1 H). Anal. Calcd for $C_{47}H_{44}ClOP_3Ru$: C, 66.08; H, 5.19. Found: C, 66.51; H, 4.81.

Synthesis of Cationic Ruthenium Hydrides (11–13). General Procedure. To a solution of hydrides **1** (chlorides) or **14a** (hexafluorophosphates) (0.2 mmol) in EtOH (10 mL) was added the bidentate phosphine (0.4 mmol). The mixture was heated under reflux conditions. The solvent was evaporated, and the residue was triturated with Et_2O and filtered off. The following cationic ruthenium hydrides were prepared as white solids in the stated yields and reaction times.

[Ru(CO)H(dppm)$_2$]PF$_6$ (11b): Reaction time 3 h; yield 80%; IR (cm^{-1}) ν(C≡O) 1980 vs; ^1H NMR (300 MHz) δ 7.50–7.40 (m, 4 H), 7.40–7.30 (m, 12 H), 7.30–7.15 (m, 24 H), 4.80 (m, 4 H), −3.68 (quintet, J = 19.7 Hz, 1H); $^{31}P\{^1H\}$ NMR δ −1.66 (s, 4 P). Anal. Calcd for $C_{51}H_{45}F_6OP_5Ru$: C, 58.68; H, 4.35. Found: C, 58.50; H, 4.20. Hydride **11a**, prepared from **1** in *ca.* 75% yield, showed identical ^1H NMR and IR, except for the ν(PF_6^-) band at 830 cm^{-1}.

[Ru(CO)H(dppe)$_2$]Cl (12a): Reaction time 16 h; yield 72%; IR (cm^{-1}) ν(C≡O) 1990 vs; ^1H NMR (300 MHz) δ 7.45–7.20 (m, 32 H), 6.99–6.96 (m, 8 H), 2.55–2.48 (m, 4 H), 2.24–2.16 (m, 4 H), −7.25 (quintet, J = 19.6 Hz, 1 H). Anal. Calcd for $C_{53}H_{49}ClOP_4Ru$: C, 66.15; H, 5.13. Found: C, 66.05; H, 5.20. Hydride **12b** was prepared from **14a** (reaction time 2 h, 89% yield) and showed identical NMR spectra. IR (cm^{-1}): ν(C≡O) 1990 vs, ν(PF_6^-) 830 vs. Anal. Calcd for $C_{53}H_{49}F_6OP_5Ru$: C, 59.39; H, 4.60. Found: C, 59.20; H, 4.42.

[Ru(CO)H(dppp)$_2$]Cl (13a): Reaction time 3 h; yield 51%; IR (cm^{-1}) ν(C≡O) 1980 vs; ^1H NMR (300 MHz) δ 7.49–6.97 (m, 40 H), 2.41–2.31 (m, 4 H), 2.28–2.18 (m, 4 H), 1.66–1.60 (m, 2 H), 1.39–1.24 (m, 2 H), −5.05 (quintet, J = 20.7 Hz, 1H). Anal. Calcd for $C_{55}H_{53}ClOP_4Ru$: C, 66.70; H, 5.39. Found: C, 66.55; H, 5.43. Hydride **13b** was prepared from **14b** (reaction time 3 h, 67% yield) and showed identical NMR spectra. IR (cm^{-1}): ν(C≡O) 1980 vs, ν(PF_6^-) 830 vs. Anal. Calcd for $C_{55}H_{53}F_6OP_5Ru$: C, 60.06; H, 4.86. Found: C, 59.96; H, 5.05.

Synthesis of Cationic Ruthenium Hydrides 15–18. General Procedure. To a solution of hydrides **14a** or **14b** (0.10 mmol) in CH_2Cl_2 (5 mL) was added the bidentate phosphine (0.10 mmol). The mixture was stirred at 23 °C for **15** and **16** and at reflux temperature for **17** and **18**. The solvent was evaporated, and the residue was triturated with

(24) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, *8*, 627.

Et_2O and filtered off. The following cationic ruthenium hydrides were prepared in the stated yields and reaction times as white solids.

[Ru(CO)H(PPh$_3$)$_2$(dppm)]PF$_6$ (15): Reaction time 1 h; yield 81%; IR (cm^{-1}) ν(C≡O) 1935 vs; ^1H NMR (300 MHz) δ 7.50–7.28 (m, 10 H), 7.28–7.12 (m, 30 H), 7.12–6.98 (m, 6 H), 6.64 (t, J = 6.9 Hz, 4 H), 2.43 (s, 2 H), 1.19 (s, 3 H), −8.02 (dtd, J = 91.7, 22.9, 3.9 Hz, 1 H); $^{31}P\{^1H\}$ NMR δ 44.65 (d, J = 15.3 Hz, 2 P), 15.78 (m, 1 P), −25.53 (d, J = 18.8 Hz, 1 P). Anal. Calcd for $C_{64}H_{54}F_6NOP_5Ru{\cdot}CH_2Cl_2$: C, 59.60; H, 4.46; N, 1.07. Found: C, 59.31; H, 4.46; N, 1.07. Found: C, 59.31; H, 4.35; N, 1.13.

[Ru(CO)H(PPh$_3$)$_2$(dppe)]ClO$_4$ (16a): Reaction time 2 h; yield 83%. Its IR and ^1H NMR spectra were almost identical to those reported for the tetrafluoroborate salt.[9] Similarly, the hexafluorophosphate (**16b**) was obtained in 85% yield. Anal. Calcd for $C_{65}H_{56}F_6P_5Ru$: C, 63.11; H, 4.56; N, 1.13. Found: C, 63.04; H, 4.61; N, 1.12.

[Ru(CO)H(PPh$_3$)(dppe)]PF$_6$ (17, 18): Reaction time 48 h; yield 82%. 2:1 mixture of **17** and **18**: ν(C≡O) 1965 vs, ν(PF_6^-) 830 vs; ^1H NMR (300 MHz) δ 7.90–6.60 (m, 35 H), 2.90–2.40 (m, 3 H), 2.16 (s, 1 H), 1.07 (s, 3 H), −6.48 (ddd, J = 93.3, 18.7, 15.2 Hz, 1H). **18**: ν(C≡O) 1960 vs ν(PF_6^-) 830 vs; ^1H NMR (300 MHz) δ 7.90–6.60 (m, 35 H), 2.90–2.40 (m, 3 H), 2.16 (s, 1 H), 1.47 (s, 3 H), −13.70 (q, J = 19.0 Hz, 1 H). Anal. Calcd for $C_{47}H_{43}F_6NOP_4Ru$: C, 57.79; H, 4.44; N, 1.43. Found: C, 57.89; H, 4.44; N, 1.23.

Ru(CO)ClH(PPh$_3$)(dppf) (19). Method a. A suspension of hydride **1** (762 mg, 0.80 mmol) and dppf (447 mg, 0.80 mmol) in EtOH (30 mL) was heated under reflux conditions for 2.5 h. After the mixture was cooled to room temperature, the solid was filtered off and washed with Et_2O and hexane to give **19** as a yellow solid (770 mg, 99%): IR (cm^{-1}) ν(C≡O) 1920 vs; ^1H NMR (300 MHz) δ 8.25 (pt, J = 8.3 Hz, 2 H), 7.92–7.84 (m, 4 H), 7.48–7.38 (m, 1 H), 7.36–7.12 (m, 18 H), 7.10–7.01 (m, 8 H), 6.84 (pt, J = 8.1 Hz, 2 H), 5.51 (br s, 1 H), 4.86 (br s, 1 H), 4.54 (br s, 1 H), 4.33 (br s, 1 H), 4.28 (br s, 2 H), 4.21 (br s, 1 H), 3.93 (br s, 1 H), −7.93 (ddd, J = 108.8, 27.7, 21.0 Hz, 1 H); $^{31}C\{^1H\}$ NMR (only carbonyl resonance) δ 202.26 (dt, J = 13.1, 9.4 Hz); $^{31}P\{^1H\}$ NMR δ 39.94 (dd, J = 305.7, 11.4 Hz, 1 P), 37.58 (dd, J = 305.7, 19.2 Hz, 1 P), 2.70 (dd, J = 19.2, 11.4 Hz, 1 P). Anal. Calcd for $C_{53}H_{44}ClFeOP_3Ru$: C, 63.60; H, 4.86. Found: C, 63.88; H, 5.02.

Method b. A solution of hydride **20** (555 mg, 0.71 mmol) and dppf (400 mg, 0.72 mmol) in toluene (15 mL) was heated under reflux conditions for 90 min. The solvent was evaporated, and the residue was triturated with Et_2O–hexane to give **19** (530 mg, 76%).

Method c. A solution of hydride **21** (493 mg, 0.64 mmol) and dppf (375 mg, 0.68 mmol) in toluene (15 mL) was heated under reflux conditions for 90 min. The solvent was evaporated, and the residue was triturated with Et_2O–hexane to give **19** (550 mg, 87%).

[Ru(CO)H(py)(PPh$_3$)(dppf)]PF$_6$ (23). A suspension of hydride **22** (1.462 g, 1.53 mmol) and dppf (867 mg, 1.56 mmol) in EtOH (80 mL) was heated under reflux conditions for 1 h. After the mixture was cooled to room temperature, the solid was filtered off and washed with EtOH, Et_2O, and hexane to give **23** as a yellow solid (1.450 g, 81%): IR (cm^{-1}) ν(C≡O) 1940 vs, ν(C=N) 1660 w, ν(PF_6) 840 vs; ^1H NMR (300 MHz) δ 7.79–7.73 (m, 4 H), 7.59–7.27 (m, 13 H), 7.18–7.04 (m, 17 H), 6.97–6.86 (m, 4 H), 6.35–6.32 (br s, 2 H), 4.92 (br s, 1 H), 4.82 (br s, 2 H), 4.61 (br s, 1 H), 4.45 (br s, 1 H), 4.29 (br s, 1 H), 4.36 (br s, 1 H), 3.48 (br s, 1 H), −8.64 (dt, J = 92.4, 25.5, 21.0 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 44.70 (dd, J = 282.6, 14.5 Hz, 1 P), 42.10 (dd, J = 282.6, 19.6 Hz, 1 P), 16.30 (dd, J = 19.6, 14.5 Hz, 1 P). Anal. Calcd for $C_{58}H_{49}F_6FeNOP_4Ru$: C, 59.50; H, 4.22; N, 1.20. Found: C, 59.39; H, 4.19; N, 1.12.

[Ru(CO)H(MeCN)(PPh$_3$)(dppf)]PF$_6$ (24). A suspension of hydride **19** (1.046 g, 1.06 mmol) and $NaPF_6$ (178 mg, 1.06 mmol) in acetonitrile (80 mL) was heated under reflux conditions for 2 h. After the mixture was cooled to room temperature, the mixture was evaporated and the residue was triturated with Et_2O to give **24** as a yellow solid (1.180 g, 98%): IR (cm^{-1}) ν(C≡O) 1940 vs, ν(PF_6) 830 vs; ^1H NMR (300 MHz) δ 7.83–7.65 (m, 4 H), 7.62–7.12 (m, 24 H), 6.98–6.85 (m, 7 H), 4.85 (br s, 1 H), 4.72 (br s, 1 H), 4.68 (br s, 1 H), 4.48 (br s, 1 H), 4.43 (br s, 1 H), 4.38 (br s, 1 H), 4.32 (br s, 1 H), 3.80 (br s, 1 H), −8.34 (ddd, J = 92.9, 26.4, 20.6 Hz, 1H); $^{31}P\{^1H\}$ NMR δ 44.26 (dd, J = 247.9, 12.3 Hz, 1 P), 39.73 (dd, J = 247.9, 18.1 Hz, 1 P), 15.94 (dd, J = 18.1, 12.3 Hz, 1 P). Anal. Calcd for $C_{55}H_{47}F_6FeNOP_4Ru$: C, 58.32; H, 4.18; N, 1.24. Found: C, 57.97; H, 4.01; N, 1.20.

Ru(CO)Cl(CH=CH-*t*-Bu)(PPh$_3$)(dppm) (25). To a suspension of hydride **2** (74 mg, 0.07 mmol) in CH_2Cl_2 (10 mL) was added 3,3-dimethyl-1-butyne (0.010 mL, 0.08 mmol). The mixture was stirred at 23 °C for 1 h. The yellow mixture was concentrated until a white precipitate appeared, and Et_2O was added to induce complete precipitation. The precipitate was filtered off and washed with Et_2O to yield **25** (52 mg, 77%) as a white solid: IR (cm^{-1}) ν(C≡O) 1950 vs; ^1H NMR (200 MHz) δ 7.88–7.78 (m, 2 H), 7.68–7.59 (m, 6 H), 7.51–7.20 (m, 18 H), 7.20–7.10 (m, 10 H), 5.32 (dd, J = 15.2, 8.0 Hz, 1 H), 4.78 (m, 2 H), 0.85 (s, 9 H); $^{31}P\{^1H\}$ NMR δ 27.59 (dd, J = 329.3, 19.8 Hz, 1 P), −2.99 (dd, J = 329.3, 13.2 Hz, 1 P), −20.18 (dd, J = 19.8, 13.2 Hz, 1P). Anal. Calcd for $C_{50}H_{48}ClOP_3Ru{\cdot}CH_2Cl_2$: C, 62.55; H, 5.11. Found: C, 62.09; H, 5.19.

Ru(CO)Cl(CH=CHPh)(PPh$_3$)(dppm) (26). Method a. To a suspension of hydride **2** (37 mg, 0.03 mmol) in CH_2Cl_2 (10 mL) was added phenylacetylene (0.025 mL, 0.23 mmol). The yellow mixture was concentrated until a white precipitate appeared, and Et_2O was added to induce complete precipitation. The precipitate was filtered off and washed with Et_2O to yield **26** (19 mg, 59%) as a yellowish solid after recrystallization (CH_2Cl_2–hexane): IR (cm^{-1}) ν(C≡O) 1955 vs, ν(C=C) 1545 vs; ^1H NMR (300 MHz) δ 8.57 (ddt, J = 16.9, 11.0, 3.0 Hz, 1H), 7.71–7.65 (m, 2 H), 7.57–7.50 (m, 6 H), 7.47–7.16 (m, 19 H), 7.14–7.04 (m, 12 H), 6.97 (t, J = 7.0 Hz, 1H), 6.32 (dd, J = 16.9, 7.0 Hz, 1H), 4.80–4.67 (m, 2 H); $^{31}P\{^1H\}$ NMR δ 28.50 (dd, J = 322.5, 19.8 Hz, 1 P), −2.37 (dd, J = 322.5, 5.5 Hz, 1 P), −20.13 (dd, J = 19.8, 5.5 Hz, 1 P). Anal. Calcd for $C_{52}H_{44}ClOP_3Ru{\cdot}H_2O$: C, 66.99; H, 4.97. Found: C, 66.93; H, 4.87.

Method b. To a suspension of hydride **1** (100 mg, 0.11 mmol) in $CHCl_3$ (10 mL) were added phenylacetylene (0.023 mL, 0.21 mmol) and dppm (50 mg, 0.13 mmol). The mixture was stirred at 23 °C for 1 h. The yellow mixture was concentrated until a white precipitate appeared, and Et_2O was added to induce complete precipitation. The precipitate was filtered off and washed with Et_2O to yield **26** (90 mg, 95%) as a white solid after recrystallization (CH_2Cl_2–hexane).

Ru(CO)Cl(CH=CH-*t*-Bu)(PPh$_3$)(dppe) (27). To a suspension of hydride **1** (100 mg, 0.11 mmol) in CH_2Cl_2 (3 mL) were added 3,3-dimethyl-1-butyne (0.026 mL, 0.21 mmol) and dppe (44 mg, 0.11 mmol). The mixture was stirred at 23 °C for 10 min. The mixture was evaporated, and the residue was triturated with Et_2O to yield **27** (79 mg, 84%) as a white solid: IR (cm^{-1}) ν(C≡O) 1960 vs; ^1H NMR (300 MHz) δ 7.93 (t, J = 7.7 Hz, 2 H), 7.77–7.60 (m, 4 H), 7.55–7.10 (m, 21 H), 7.06–6.96 (m, 7 H), 6.95–6.82 (m, 2 H), 5.10 (dd, J = 16.8, 6.8 Hz, 1 H), 2.74–2.48 (m, 3 H), 2.35 (s, 1 H), 0.78 (s, 9 H); $^{31}P\{^1H\}$ NMR δ 41.64 (d, J = 320.5 Hz, 1 P), 25.23 (d, J = 18.3 Hz, 1 P), 23.15 (dd, J = 320.5, 18.2 Hz, 1 P). Anal. Calcd for $C_{51}H_{50}ClOP_3Ru$: C, 67.43; H, 5.55. Found: C, 67.65; H, 5.84.

Ru(CO)Cl(CH=CH-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppe) (28). To a suspension of hydride **1** (100 mg, 0.11 mmol) in CH_2Cl_2 (6 mL) were added *p*-tolylacetylene (0.020 mL, 0.15 mmol) and dppe (84 mg, 0.21 mmol). The mixture was stirred at 23 °C for 10 min. The mixture was evaporated, and the residue was triturated with Et_2O to yield **28** (88 mg, 81%) as a white solid: IR (cm^{-1}) ν(C≡O) 1958 vs, ν(C=C) 1543 vs; ^1H NMR (200 MHz) δ 8.26 (dd, J = 16.8, 8.7 Hz, 1 H), 7.82–7.75 (m, 2 H), 7.74–7.63 (m, 2 H), 7.62–7.46 (m, 3 H), 7.45–7.09 (m, 22

H), 7.08–6.86 (m, 10 H), 5.94 (ddd, J = 16.8, 6.5, 2.5 Hz, 1 H), 2.73–2.30 (m, 4 H), 2.28 (s, 3 H); $^{31}P\{^1H\}$ NMR δ 43.65 (d, J = 314.2 Hz, 1 P), 28.10 (d, J = 18.5 Hz, 1 P), 25.29 (dd, J = 314.2, 18.5 Hz, 1 P). Anal. Calcd for $C_{54}H_{48}ClOP_3Ru$: C, 68.82; H, 5.13. Found: C, 68.98; H, 4.97.

Ru(CO)Cl(CH=CH-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppp) (29). To a suspension of hydride **1** (100 mg, 0.11 mmol) in CH_2Cl_2 (6 mL) were added *p*-tolylacetylene (0.020 mL, 0.153 mmol) and dppp (53 mg, 0.13 mmol). The mixture was stirred at 23 °C for 10 min. The mixture was evaporated, and the residue was triturated with Et_2O and hexane to yield **29** (76 mg, 69%) as a white solid: IR (cm^{-1}) ν(C≡O) 1938 vs, ν(C=C) 1548 vs; ^1H NMR (200 MHz) δ 8.32–8.16 (m, 1 H), 7.88–7.82 (m, 2 H), 7.51–6.80 (m, 37 H), 6.77 (pd, J = 7.2 Hz, 2 H), 6.13 (dd, J = 16.8, 6.5 Hz, 1 H), 2.70–2.50 (m, 3 H), 2.40–2.30 (m, 2 H), 2.24 (s, 3 H), 2.20–2.10 (m, 1 H); $^{31}P\{^1H\}$ NMR δ 24.94 (dd, J = 308.5, 19.3 Hz, 1 P), 10.42 (dd, J = 308.5, 19.3 Hz, 1 P), −11.54 (t, J = 19.3 Hz, 1 P). Anal. Calcd for $C_{55}H_{50}ClOP_3Ru \cdot {}^1/_2CH_2Cl_2$: C, 66.73; H, 5.15. Found: C, 66.65; H, 4.97.

Ru(CO)Cl(CH=CH-*t*-Bu)(PPh$_3$)(dppf) (30). Method a. A solution of alkenyl **33** (720 mg, 0.85 mmol) and dppf (470 mg, 0.85 mmol) in toluene (15 mL) was heated under reflux conditions for 90 min. The solvent was evaporated, and the residue was triturated with Et_2O and hexane to give **30** as a yellow solid (625 mg, 69%): IR (cm^{-1}) ν(C≡O) 1925 vs; ^1H NMR (300 MHz) δ 8.75–8.70 (m, 2 H), 7.92 (pt, J = 7.8 Hz, 2 H), 7.51–6.90 (m, 29 H), 6.55 (t, J = 7.9 Hz, 2 H), 6.34 (ddt, J = 16.6, 12.3, 4.2 Hz, 1 H), 5.62 (br s, 1 H), 5.06 (br s, 1 H), 5.02 (ddt, J = 16.6, 7.4, 2.4 Hz, 1 H), 4.24 (br s, 1 H), 4.10 (br s, 1 H), 4.05 (br s, 1 H), 4.04 (br s, 1 H), 3.68 (br s, 1), 3.63 (br s, 1 H), 0.51 (s, 9 H); $^{31}P\{^1H\}$ NMR δ 22.96 (dd, J = 333.8, 17.6 Hz, 1 P), 18.36 (dd, J = 338.8, 8.6 Hz, 1 P), −5.40 (dd, J = 17.6, 8.6 Hz, 1 P). Anal. Calcd for $C_{59}H_{54}FeClOP_3Ru \cdot H_2O$: C, 65.47; H, 5.22. Found: C, 65.74; H, 5.32.

Method b. A solution of alkenyl **34** (496 mg, 0.64 mmol) and dppf (364 mg, 0.66 mmol) in CH_2Cl_2 (15 mL) was heated under reflux conditions for 1 h. The solvent was evaporated, and the residue was triturated to give **30** (470 mg, 69%).

Ru(CO)Cl(CH=CH-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppf) (31). A solution of alkenyl **33** (164 mg, 0.18 mmol) and dppf (108 mg, 0.19 mmol) in toluene (10 mL) was heated under reflux conditions for 90 min. The solvent was evaporated, and the residue was triturated with Et_2O and hexane to give **31** as a yellow solid (120 mg, 59%): IR (cm^{-1}) ν(C≡O) 1925 vs; ^1H NMR (200 MHz) δ 8.75–8.69 (m, 2 H), 7.90 (pt, J = 7.5 Hz, 2 H), 7.56–6.86 (m, 32 H), 6.77 (d, J = 8.0 Hz, 2 H), 6.54 (t, J = 8.0 Hz, 2 H), 6.07 (ddm J = 17.1, 6.7 Hz, 1 H), 5.84 (br s, 1 H), 5.10 (br s, 1 H), 4.19 (br s, 1 H), 4.16 (br s, 1 H), 4.05 (br s, 1 H), 4.02 (br s, 1 H), 3.66 (br s, 1 H), 3.54 (br s, 1 H), 2.22 (s, 3 H). Anal. Calcd for $C_{62}H_{52}ClFeOP_3Ru$: C, 67.80; H, 4.77. Found: C, 67.60; H, 4.91.

Ru(CO)Cl(CH=CH-*t*-Bu)(Me$_2$Hpz)(dppf) (37). A solution of alkenyl **35** (617 mg, 0.78 mmol) and dppf (440 mg, 0.79 mmol) in toluene (15 mL) was heated under reflux conditions for 40 min. The solvent was evaporated, and the residue was triturated with Et_2O to give **37** as a yellow solid (500 mg, 71%): IR (cm^{-1}) ν(NH) 3200 m, ν(C≡O) 1920 vs, ν(C=N) 1570 m; ^1H NMR (200 MHz) δ 11.46 (s, 1 H), 7.90–7.64 (m, 5 H), 7.43–7.01 (m, 15 H), 6.55 (ddd, J = 16.3, 9.3, 4.2 Hz, 1 H), 5.54–5.49 (m, 2 H), 5.04 (ddd, J = 16.3, 7.5, 0.8 Hz, 1 H), 4.79–4.76 (m, 1H), 4.57–4.54 (m, 1 H), 4.50–4.46 (m, 1 H), 4.40–4.37 (m, 1 H), 4.32–4.29 (m, 1 H), 4.27–4.24 (m, 1 H), 4.16–4.13 (m, 1 H), 2.02 (s, 3 H), 1.81 (s, 3 H), 0.76 (s, 9 H); $^{31}P\{^1H\}$ NMR δ 41.16 (d, J = 12 Hz, 1 P), 10.92 (J = 12 Hz, 1 P). Anal. Calcd for $C_{46}H_{47}ClFeN_2OP_2Ru \cdot H_2O$: C, 60.30; H, 5.39; N, 3.05. Found: C, 60.27; H, 4.65; N, 2.81.

Ru(CO)Cl(CH=CH-*p*-MeC$_6$H$_4$)(Me$_2$Hpz)(dppf) (38). A solution of alkenyl **37** (790 mg, 0.87 mmol) and dppf (492 mg, 0.89 mmol) in toluene (15 mL) was heated under reflux conditions for 40 min. The solvent was evaporated, and the residue was triturated with Et_2O to give **38** as a yellow solid (670 mg, 82%): IR (cm^{-1}) ν(NH) 3200 m, ν(C≡O) 1920 vs, ν(C=N) 1570; ^1H NMR (200 MHz) δ 11.60 (s, 1 H), 7.92 (ddd, J = 16.8, 8.4, 3.4 Hz, 1 H), 7.80–7.68 (m, 5 H), 7.58–7.49 (m, 5 H), 7.37–7.04 (m, 14 H), 6.09 (dd, J = 16.8, 7.1 Hz, 1 H), 5.50 (s, 1 H), 5.24 (br s, 1 H), 4.89 (br s, 1 H), 4.50 (s, 1 H), 4.42 (br s, 1 H), 4.36 (br s, 1 H), 4.34 (br s, 1 H), 4.26 (br s, 1 H), 2.23 (s, 3 H), 1.97 (s, 3 H), 1.81 (s, 3 H); $^{13}C\{^1H\}$ NMR (only significant signals) δ 205.00 (dd, J = 19.4, 8.1 Hz, CO), 156.15 (dd, J = 82.8, 15.4 Hz, CH=), 81.77 (dd, J = 45.6, 7.0 Hz, CH=); $^{31}P\{^1H\}$ NMR δ 40.27 (d, J = 13 Hz, 1 P), 10.03 (J = 13 Hz, 1 P). Anal. Calcd for $C_{49}H_{45}ClFeN_2OP_2Ru \cdot H_2O$: C, 61.94; H, 4.98; N, 2.94. Found: C, 61.99; H, 5.04; N, 2.86.

Ru(CO)Cl(C≡C-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppm) (39). To a solution of alkenyl complex **25** (127 mg, 0.14 mmol) in 1,2-dichloroethane (12 mL) was added *p*-tolylacetylene (0.086 mL, 0.68 mmol). The mixture was heated under reflux conditions for 12 h. The mixture was evaporated, and hexane was added to give a yellowish solid which was filtered off and washed with Et_2O to yield **39** (107 mg, 81%): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1964 vs; ^1H NMR (300 MHz) δ 8.36–8.28 (m, 1 H), 7.89–7.97 (m, 4 H), 7.74–7.63 (m, 3 H), 7.42–7.32 (m, 5 H), 7.31–7.07 (m, 22 H), 7.05 (pd, J = 8.5 Hz, 2 H), 6.97 (pd, J = 8.5 Hz, 2H), 4.83–4.66 (m, 2 H), 2.29 (s, 3 H). Anal. Calcd for $C_{53}H_{44}ClOP_3Ru$: C, 68.72; H, 4.79. Found: C, 68.81; H, 4.82.

Ru(CO)Cl(C≡C-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppe) (40). Method a. To a solution of hydride **6** (71 mg, 0.08 mmol) in 1,2-dichloroethane (12 mL) was added *p*-tolylacetylene (0.032 mL, 0.26 mmol). The mixture was heated under reflux conditions for 17 h. The mixture was concentrated, and Et_2O was added to give a gray suspension which was filtered. Et_2O and hexane were added to the solution to give a white precipitate, which was filtered off and washed with Et_2O to yield **40** (47 mg, 58%): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1980 vs; ^1H NMR (200 MHz) δ 8.32–8.24 (m, 2 H), 8.23–7.97 (m, 2 H), 7.67–7.57 (m, 8 H), 7.34–7.24 (m, 9 H), 7.23–7.12 (m, 6 H), 7.09–6.98 (m, 8 H), 6.92 (s, 4 H), 2.72–2.26 (m, 4 H), 2.27 (s, 3 H); $^{31}P\{^1H\}$ NMR δ 44.475 (dd, J = 324.4, 9.7 Hz, 1 P), 33.29 (dd, J = 21.2, 9.7 Hz, 1 P), 24.57 (dd, J = 323.5, 21.2 Hz, 1 P). Anal. Calcd for $C_{54}H_{46}ClOP_3Ru$: C, 68.97; H, 4.93. Found: C, 68.85; H, 4.97.

Method b. To a solution of **27** (100 mg, 0.11 mmol) in 1,2-dichloroethane (12 mL) was added *p*-tolylacetylene (0.028 mL, 0.22 mmol). The mixture was heated under reflux conditions for 4 h and stirred at 23 °C for 16 h. The mixture was concentrated, and Et_2O was added to give a gray suspension which was filtered. Et_2O and hexane were added to the solution to give a white precipitate, which was filtered off and washed with Et_2O to yield **40** (83 mg, 80%).

Ru(CO)Cl(C≡C-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppp) (41). To a solution of hydride **7** (75 mg, 0.089 mmol) in 1,2-dichloroethane (10 mL) was added *p*-tolylacetylene (0.015 mL, 0.27 mmol). The mixture was heated under reflux conditions for 4 h. After the mixture was cooled to room temperature, Et_2O was added to give a white suspension, which was filtered. The solution was concentrated to give a beige suspension. The solid was filtered off and washed with hexane to yield **41** (33 mg, 39%): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1953 vs; ^1H NMR (200 MHz) δ 8.06–7.88 (m, 4 H), 7.65 (t, J = 8.2 Hz, 3 H), 7.49–6.89 (m, 28 H), 6.76 (pd, J = 7.9 hz, 2 H), 6.34 (pd, J = 7.9 Hz, 2 H), 3.09–2.75 (m, 3 H), 2.69–2.26 (m, 2 H), 2.20 (s, 3 H), 2.12–1.87 (m, 1 H); $^{31}P\{^1H\}$ NMR δ 30.29 (dd, J = 317.3, 23.3 Hz, 1 P), 11.51 (dd, J = 317.3, 28.4 Hz, 1 P), −0.80 (dd, J = 317.3, 23.3 Hz, 1 P). Anal. Calcd for $C_{55}H_{48}ClOP_3Ru \cdot H_2O$: C, 67.93; H, 5.18. Found: C, 67.27; H, 5.18.

Ru(CO)Cl(C≡C-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppb) (42). To a solution of hydride **8** (26 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was added *p*-tolylacetylene (0.015 mL, 0.27 mmol). The mixture was stirred at 23 °C for 24 h. The mixture was evaporated, and the residue was triturated with Et_2O and washed with hexane to yield **42** (17 mg, 35%). A satisfactory microanalysis was not obtained for this complex: IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1975 vs; ^1H NMR (200 MHz) δ 8.20–7.88 (m, 4 H),

Table 2. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for Hydride 19

Crystal Data	
formula	$C_{53}H_{44}ClOP_3FeRu$
fw	982.22
cryst size, mm	0.10 × 0.10 × 0.20
cryst system	monoclinic
space group	$P2_1/n$
a, Å	15.768(1)
b, Å	25.252(2)
c, Å	11.213(1)
β, deg	92.83(1)
V, Å^3	4459.3(6)
Z	4
d_{calcd}, g cm^{-3}	1.4630
$F(000)$	2008
μ, cm^{-1}	73.30
Data Collection Parameters	
diffractometer	four-circle Philips PW 1100
radiation (λ, Å)	monochromated Cu Kα (1.541 78)
T, K	296
θ max, deg	65
scan technique	$\omega/2\theta$
cryst decay	no
Structure Determination and Refinement	
no. of measd reflns	8013
no. of ind reflns	7606
no. of obsd reflns	3284 ($I \geq 4\sigma(I)$ criterion)
abs corr	applied[a]
min, max absorption correction	0.865, 1.252
no. of variables	541
max $\Delta\rho$, e/Å^3	1.07
final R and R_w, %	6.8, 6.7

[a] Reference 25.

7.65 (t, J = 8.2 Hz, 3 H), 7.49–6.89 (m, 28 H), 6.75 (pd, J = 7.9 Hz, 2 H), 6.28 (pd, J = 7.9 Hz, 2 H), 3.09–2.75 (m, 3 H), 2.69–2.50 (m, 2 H), 2.48–1.75 (m, 6 H), 2.20 (s, 3 H).

Ru(CO)Cl(C≡C-*p*-MeC$_6$H$_4$)(PPh$_3$)(dppf) (43). Method a. To a solution of alkenyl **30** (156 mg, 0.15 mmol) in CH_2Cl_2 (6 mL) was added *p*-tolylacetylene (50 μL, 0.39 mmol). The mixture was stirred at 23 °C for 24 h. The mixture was evaporated, and the residue was triturated with Et_2O and washed with hexane to yield **43** (120 mg, 75%): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1960 vs; ^{1}H NMR (200 MHz) δ 8.45 (pt, J = 8.8 Hz, 2 H), 8.30–8.25 (m, 2 H), 8.04–8.01 (m, 2 H), 7.53–6.92 (m, 27 H), 6.82 (d, J = 7.9 hz, 2 H), 6.70 (pt, J = 8.1 Hz, 2 H), 6.56 (pd, J = 7.9 Hz, 2 H), 5.39 (br s, 1 H), 4.89 (br s, 1 H), 4.51 (br s, 1 H), 4.30 (br s, 1 H), 4.24 (br s, 1 H), 4.19 (br s, 1 H), 4.16 (br s, 1 H), 3.88 (br s, 1 H), 2.22 (s, 3 H); ^{31}P{^{1}H} NMR δ 23.90 (dd, J = 343.9, 20.3 Hz, 1 P), 20.81 (dd, J = 343.9, 20.7 Hz, 1 P), −0.85 (dd, J = 20.7, 20.3 Hz, 1 P). Anal. Calcd for $C_{62}H_{52}ClFeOP_3Ru\cdot H_2O$: C, 65.59; H, 5.03. Found: C, 65.57; H, 4.93.

Method b. To a suspension of hydride **19** (341 mg, 0.35 mmol) in EtOH (10 mL) was added *p*-tolylacetylene (0.20 mL, 1.88 mmol), and the resulting mixture was heated under reflux conditions for 48 h. Additional *p*-tolylacetylene (0.10 mL, 0.94 mmol) was added after 24 h. After the mixture was to room temperature, the solid was filtered off, washed with Et_2O, and dried to give **43** (189 mg, 54%).

Ru(CO)Cl(C≡C-*t*-Bu)(PPh$_3$)(dppf) (44). To a solution of alkenyl complex **30** (162 mg, 0.15 mmol) in CH_2Cl_2 (8 mL) was added *p*-tolylacetylene (50 μL, 0.41 mmol). The mixture was stirred at 23 °C for 24 h. The mixture was evaporated, and the residue was triturated with Et_2O and washed with hexane to yield **44** (120 mg, 74%): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1960 vs; ^{1}H NMR (200 MHz) δ 8.45–8.30 (m, 4 H), 8.10–8.05 (m, 2 H), 7.54–6.92 (m, 27 H), 6.72 (pt, J = 8.3 Hz, 2 H), 5.14 (br s, 1 H), 4.85 (br s, 1 H), 4.42 (br s, 1 H), 4.17 (br s, 1 H), 4.13 (br s, 2 H), 4.06 (br s, 1 H), 3.97 (br s, 1 H), 0.66 (s, 9 H); ^{31}P{^{1}H} NMR δ 25.49 (dd, J = 347.9, 19.5 Hz, 1 P), 21.68 (dd, J = 347.9, 20.9 Hz, 1 P), 0.11 (dd, J = 20.9, 19.5 Hz, 1 P). Anal. Calcd for $C_{59}H_{52}ClFeOP_3Ru\cdot H_2O$: C, 65.59; H, 5.03. Found: C, 65.67; H, 5.03.

Ru(CO)Cl(C≡C-*p*-MeC$_6$H$_4$)(Me$_2$Hpz)(dppf) (45). To a solution of alkenyl complex **37** (168 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) was added *p*-tolylacetylene (25 μL, 0.20 mmol). The mixture was stirred at 23 °C for 40 h. The mixture was evaporated, and the residue was triturated with Et_2O and washed with hexane to yield **45** (140 mg, 80%): IR (cm^{-1}) ν(NH) 3200 m, ν(C≡C) 2100 m, ν(C≡O) 1940 vs, ν(C=N) 1570 m; ^{1}H NMR (300 MHz) δ 11.40 (s, 1 H), 8.28–8.19 (m, 4 H), 7.50–7.10 (m, 16 H), 6.93 (pd, J = 8.1 Hz, 2 H), 6.86 (pd, J = 8.1 Hz, 2 H), 5.66 (s, 1 H), 5.45 (br s, 1 H), 4.89 (br s, 1 H), 4.69 (br s, 1 H), 4.54 (br s, 1 H), 4.42 (br s, 1 H), 4.35 (br s, 1 H), 4.33 (br s, 1 H), 4.07 (br s, 1 H), 2.23 (s, 3 H), 2.20 (s, 3 H), 1.87 (s, 3 H); ^{31}P{^{1}H} NMR δ 39.25 (d, J = 18.6 Hz, 1 P), 16.04 (d, J = 18.6 Hz, 1 P). Anal. Calcd for $C_{49}H_{43}N_2ClFeOP_2Ru\cdot H_2O$: C, 62.07; H, 4.78; N, 2.95. Found: C, 62.16; H, 4.71; N, 2.78.

Ru(CO)Cl(PPh$_3$)(dppf)(CH=CH-*p*-C$_6$H$_4$-CH=CH)Ru(CO)Cl(PPh$_3$)(dppf) (46). Method a. To a solution of hydride **1** (189 mg, 0.20 mmol) in CH_2Cl_2 (15 mL) was added *p*-diethynylbenzene (13 mg, 0.11 mmol). To the red solution was added dppf (116 mg, 0.21 mmol), and the mixture was stirred at 23 °C for 20 min and under reflux conditions for 30 min. Addition of Et_2O led to the formation of a yellow solid, which was filtered off and washed with Et_2O and hexane to give a 1:1 mixture of **46a** and **46b** as a yellow solid (161 mg, 77%): IR (cm^{-1}) ν(C≡O) 1920 vs; ^{1}H NMR (200 MHz) δ 8.90–8.56 (m, 2 H), 8.20–7.68 (m, 4 H), 7.75–6.79 (m, 62 H), 6.78–6.57 (m, 4 H), 6.50 (pd, J = 8.1 Hz, 4 H), 6.13 (ddt, J = 17.0, 6.9, 3.2 Hz, 2 H), 5.86 (s, 2 H), 5.09 (s, 2 H), 4.20–4.15 (m, 4 H), 4.3–4.01 (m, 4 H), 3.66 (br s, 2 H), 3.53 (s, 2 H); ^{31}P{^{1}H} NMR showed two ABX systems: δ_A = 21.53, δ_B = 19.67, δ_X = −3.70 (J_{AB} = 333.8, J_{AX} = 19.0, J_{BX} = 9.2 Hz); $\delta_{A'}$ = 21.91, $\delta_{B'}$ = 19.38, $\delta_{X'}$ = −3.66 ($J_{A'B'}$ = 334.2, $J_{A'X'}$ = 17.7, $J_{B'X'}$ = 9.9 Hz). Anal. Calcd for $C_{116}H_{94}Cl_2Fe_2O_2P_6Ru_2\cdot H_2O$: C, 66.07; H, 4.59. Found: C, 65.70; H, 4.63.

Method b. Complex **46** could also be prepared from **47** in higher yield by reaction with 2 equiv of dppf as follows: To a solution of **47** (316 mg, 0.21 mmol) in CH_2Cl_2 (30 mL) was added dppf (245 mg, 0.42 mmol). The resulting mixture was heated under reflux conditions until the color changed from red to yellow (*ca.* 4 h). After being cooled to room temperature, the mixture was concentrated (*ca.* 10 mL) and treated with Et_2O until a yellow precipitated appeared. The solid was filtered off and washed with Et_2O and hexane to give complex **46** (373 mg, 85%). Complex **47** was synthesized as follows: To a solution of hydride **1** (379 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) was added *p*-diethynylbenzene (26 mg, 0.21 mmol), and the resulting mixture was stirred at 23 °C for 90 min. The solvent was evaporated, and the residue was triturated with Et_2O to give **47** as a dark red microcrystalline solid (400 mg, quantitative): IR (cm^{-1}) ν(C≡O) 1930 vs; ^{1}H NMR (300 MHz) δ 8.25 (dt, J = 13.3, 2.2 Hz, 2 H), 7.60–7.51 (m, 24 H), 7.42–7.34 (m, 36 H), 6.56 (s, 4 H), 5.57 (dt, J = 13.2, 1.9 Hz, 2 H); ^{31}P{^{1}H} NMR δ 31.08 (s, 4 P). Anal. Calcd for $C_{84}H_{68}Cl_2O_2P_4Ru_2$: C, 66.98; H, 4.55. Found: C, 65.60; H, 4.50.

Ru(CO)Cl(PPh$_3$)(dppf)(C≡C-*p*-C$_6$H$_4$-C≡C)Ru(CO)Cl(PPh$_3$)(dppf) (48). To a solution of alkenyl complex **30** (169 mg, 0.16 mmol) in CH_2Cl_2 (6 mL) was added *p*-diethynylbenzene (10 mg, 0.08 mmol). The mixture was stirred at 23 °C for 40 h. The mixture was evaporated, and the residue was triturated with Et_2O and washed with hexane to yield a 1:1 mixture of **47a** AND **47b** as a yellow solid (120 mg, 73%): IR (cm^{-1}) ν(C≡C) 2100 m, ν(C≡O) 1960 vs; ^{1}H NMR (300 MHz) δ 8.45 (pt, J = 8.7 Hz, 4 H), 8.30–8.20 (m, 4 H), 8.00–7.95 (m, 8 H), 7.49–6.88 (m, 54 H), 6.69 (pt, J = 8.1 Hz, 4 H), 6.30 (s, 4 H), 5.38 (br s, 2 H), 4.88 (br s, 2 H), 4.49 (br s, 2 H), 4.29 (br s, 2 H), 4.22 (br s, 2 H), 4.17 (br s, 4 H), 3.87 (br s, 2 H). ^{31}P{^{1}H} NMR showed two ABX systems: δ_A = 22.83, δ_B = 21.52, δ_X = −0.71 (J_{AB} = 345.4, J_{AX} = 20.9, J_{BX} = 18.7 Hz); $\delta_{A'}$ = 22.82, $\delta_{B'}$ = 21.53, $\delta_{X'}$ = −0.77 ($J_{A'B'}$ = 345.8, $J_{A'X'}$ = 21.1

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³) for Non-Hydrogen Atoms for Hydride 19

atom	x	y	z	U(eq)[a]	atom	x	y	z	U(eq)[a]
Ru	2731(1)	3957(1)	6729(1)	45(1)	C(202)	2987(9)	2806(7)	3620(13)	69(6)
C(1)	3367(10)	3970(7)	8137(15)	70(6)	C(203)	3172(14)	2832(9)	2407(18)	105(9)
O(1)	3743(7)	3970(6)	8991(10)	86(5)	C(204)	3794(13)	3139(10)	2078(16)	98(9)
Cl	1893(2)	3975(2)	4802(3)	61(1)	C(205)	4237(11)	3457(8)	2868(19)	87(8)
Fe	1763(1)	2408(1)	7507(2)	50(1)	C(206)	4061(9)	3464(6)	4064(15)	72(6)
C(10)	2414(8)	2574(5)	6061(10)	50(5)	C(211)	4147(8)	2798(6)	6613(12)	55(5)
C(11)	2534(9)	2032(5)	6389(13)	59(6)	C(212)	4509(9)	2375(6)	6022(12)	61(5)
C(12)	1716(10)	1773(6)	6368(14)	66(6)	C(213)	5263(10)	2129(7)	6474(15)	73(7)
C(13)	1128(9)	2152(7)	5988(13)	67(6)	C(214)	5652(12)	2309(9)	7463(18)	109(9)
C(14)	1535(7)	2654(5)	5801(11)	48(5)	C(215)	5351(17)	2739(13)	7973(20)	203(16)
C(20)	1599(9)	3051(5)	8558(11)	50(5)	C(216)	4591(14)	2989(8)	7583(17)	128(10)
C(21)	909(9)	2675(6)	8671(12)	63(6)	P(3)	2704(2)	4895(1)	6721(3)	52(1)
C(22)	1263(11)	2190(6)	9090(13)	68(6)	C(301)	3366(8)	5185(5)	7946(12)	48(5)
C(23)	2144(11)	2255(6)	9252(13)	72(7)	C(302)	4183(9)	5321(6)	7845(13)	58(6)
C(24)	2361(10)	2789(6)	8914(12)	60(6)	C(303)	4462(8)	5523(6)	8848(16)	69(6)
P(1)	1509(2)	3720(1)	7992(3)	48(1)	C(304)	4314(11)	5571(6)	9931(13)	65(6)
C(101)	1540(7)	4104(5)	9392(10)	43(5)	C(305)	3505(11)	5439(6)	10040(13)	73(7)
C(102)	1103(8)	4592(5)	9470(12)	52(5)	C(306)	3026(9)	5227(7)	9047(14)	75(7)
C(103)	1151(10)	4871(6)	10536(14)	68(6)	C(311)	1702(8)	5264(5)	6828(13)	55(5)
C(104)	1631(12)	4695(9)	11501(14)	88(8)	C(312)	970(9)	5026(5)	6402(11)	55(5)
C(105)	2044(10)	4220(8)	11407(15)	79(7)	C(313)	193(9)	5279(6)	6448(13)	64(6)
C(106)	1998(9)	3915(6)	10379(12)	64(6)	C(314)	149(11)	5772(7)	6955(16)	86(7)
C(111)	372(8)	3747(5)	7552(12)	51(5)	C(315)	872(10)	6003(8)	7352(18)	111(9)
C(112)	−233(9)	3729(6)	8452(12)	62(5)	C(316)	1659(10)	5765(7)	7303(18)	101(8)
C(113)	−1120(9)	3726(7)	8179(16)	81(7)	C(321)	3152(8)	5195(5)	5394(12)	52(5)
C(114)	−1360(10)	3750(8)	6990(18)	96(8)	C(322)	3368(11)	4898(7)	4426(15)	84(7)
C(115)	−805(11)	3773(8)	6098(17)	97(8)	C(323)	3714(13)	5134(8)	3430(16)	99(9)
C(116)	77(10)	3771(6)	6394(12)	72(6)	C(324)	3846(11)	5664(8)	3426(13)	78(7)
P(2)	3165(2)	3109(1)	6030(3)	45(1)	C(325)	3634(13)	5952(7)	4329(14)	96(8)
C(201)	3410(8)	3129(5)	4414(12)	50(5)	C(326)	3248(12)	5735(6)	5314(13)	86(7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$J_{BX'}$ = 18.8 Hz). Anal. Calcd for $C_{116}H_{90}Cl_2Fe_2O_2P_6Ru_2$: C, 66.77; H, 4.35. Found: C, 66.56; H, 4.25.

X-ray Data Collection, Structure Determination, and Refinement of 19. Crystals of **19** were grown from a 1:1 CH_2Cl_2–Et_2O solution. A single pale orange crystal was selected. The determination of the cell constants and the intensity data collection were carried out at room temperature. Unit cell constants were determined by least-squares refinement of 49 accurately centered reflections. Crystal analysis parameters are listed in Table 2. The structure was solved by Patterson and Fourier synthesis. The positional coordinates and thermal parameters for the non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were isotropically refined. Atomic coordinates are listed in Table 3. The structure was solved by the heavy-atom method. The Ru and Fe atoms were identified in the Patterson map, and the other atoms, by a subsequent Fourier synthesis. After isotropic refinement (R = 0.096), an empirical absorption correction was applied[25] with minimum and maximum corrections being 0.865 and 1.252, respectively. A subsequent difference Fourier synthesis allowed the identification of the hydrogen atoms. The final cycle of anisotropic treatment of the non-hydrogen atoms included 541 variable parameters and converged to the unweighted and weighted factors of R = 6.8 and R_w = 6.7%. The relatively high R value can be explained by the low data to parameter ratio due to the small size of the crystals obtained. The largest residual peak on the final difference Fourier is 1.07 e/Å³ near the Fe atom. All calculations used the full matrix and were carried out on a VAX 6410 computer by using the following programs: XRAY80 System,[26a] DIRDIF,[26b] and PARST.[26c] Scattering and anomalous dispersion factors were taken from the literature.[27] The final positional and thermal parameters are listed in Table 3.

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Supplementary Material Available: Tables of calculated atomic coordinates, anisotropic thermal parameters, complete bond lengths and angles, torsion angles, least-squares planes, and intermolecular contacts (19 pages). Ordering information is given on any current masthead page.

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