Metallacycle Expansion by Alkyne Insertion. Chemistry of a New Family of Ruthenium Organometallics

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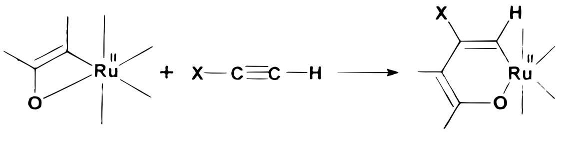
Acetylene and phenylacetylene reacts with carbonylchloro[4-methyl-6-((R-imino)methyl)-phenolato-*C*,*O*]bis(triphenylphosphine)ruthenium(II), Ru(RL^1)(PPh_3)$_2$(CO)Cl (**3**), affording the inserted product carbonylchloro[2-vinyl-4-methyl-6-((R-imino)methyl)phenolato-*C*,*O*]bis-(triphenylphosphine)ruthenium(II), Ru(RL^2,X)(PPh_3)$_2$(CO)Cl (**4**), in virtually quantitative yield. The X-ray structures of **4b** (R = X = Ph) and **4g** (R = Et, X = H) have revealed the presence of distorted-octahedral RuC_2P_2ClO coordination spheres. In the conversion **3** → **4**, the Ru(C,O) chelate ring expands from four-membered to six-membered. The insertion of phenylacetylene is regiospecific, and a reaction model implicating initial Ru−O cleavage and steric control is proposed. The Ru−O bond in **4** is significantly shorter (by ∼0.14 Å) and stronger than that in **3**. This is reflected in the lowering of the ruthenium(III)−ruthenium(II) reduction potential by ∼200 mV. The uncoordinated Schiff base moiety in **4** is present in the hydrogen-bonded iminium−phenolato zwitterionic form, as revealed by the N···O distance as well as by IR and NMR data.

Introduction

The insertion of atoms and small unsaturated molecules into metal−carbon bonds is of abiding interest in chemical research. In the particular case of alkyne insertion—a reaction first observed in the form of metal-promoted oligomerization[1,2]—the net outcome of the primary process and secondary reactions that frequently follow is the formation of new metal−carbon, carbon−carbon, and/or carbon−nonmetal bonds. This makes alkyne insertion a potentially versatile tool for organometallic and organic synthesis.[3−8]

The concern of the present work is alkyne insertion into ruthenium−carbon bonds, several instances of which are known.[2,3d,9−13] Herein we describe the new insertion reaction stated in eq 1, where the four-membered metallacycle **1** is expanded to the six-membered type **2**. The structure and properties of a family of hitherto unknown organometallics incorporating **2** are reported. The pathway of the reaction of eq 1 is scrutinized.



(1)

1 **2**

Results and Discussion

The New Family. The precursor complexes incorporating the chelate ring **1** are of the type Ru(RL^1)-(PPh_3)$_2$(CO)Cl (**3**), formed by decarbonylative metalation of 4-methyl-2,6-diformylphenol by Ru(PPh_3)$_3$$Cl_2$ in the

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[3] Some representative examples are cited in refs 3−7 according to the metal in the M−C bond undergoing insertion. Pd−C: (a) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550. (b) Larock, R. C.; Doty, M. J.; Cacchi, S. *J. Org. Chem.* **1993**, *58*, 4579. (c) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509. (d) Spencer, J.; Pfeffer, M.; Kyritsakas, N.; Fischer, J. *Organometallics* **1995**, *14*, 2214. (e) Pfeffer, M. *Pure Appl. Chem.* **1992**, *64*, 335. (f) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S.-E.; Borgne, G. L. *J. Chem. Soc., Dalton Trans.* **1979,** 547. (g) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535. (h) Ossor, H.; Pfeffer, M.; Jastrzebski, J. T. B. H.; Stam, C. H. *Inorg. Chem.* **1987**, *26*, 1169.

[4] V−C: (a) Buijink, J. K. F.; Kloeststra, K. R.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 2523. (b) Moore, M.; Gambarotta, S.; Yap, G.; Liable-Sands, L. M.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1997**, 643.

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[6] Fe−C: Butler, I. R. *Can. J. Chem.* **1990**, *68*, 1979.

[7] Ni−C: (a) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1994**, *13*, 3767. (b) Carmona, E.; Gutierrez-Puebla, E.; Monge, A.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1989**, *8*, 967. (c) Martinez, M.; Muller, G.; Panyella, D.; Rocamora, M.; Solans, X.; Font-Bardia, M. *Organometallics* **1995**, *14*, 5552. (d) Arlen, C.; Pfeffer, M.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1983**, 928.

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[13] Lutsenko, Z. L.; Aleksandrov, G. G.; Petrovskii, P. V.; Shubina, E. S.; Andrianov, V. G.; Struchkov, Yu. T.; Rubezhov, A. Z. *J. Organomet. Chem.* **1985**, *281*, 349.

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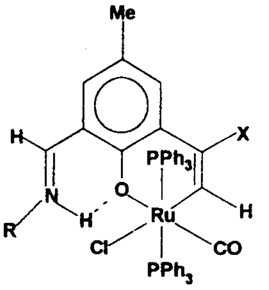
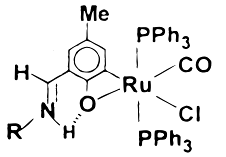


	R	X
4a	Me	H
4b	Et	H
4c	p-MeC$_6$H$_4$	H
4d	p-ClC$_6$H$_4$	H
4e	Me	Ph
4f	Et	Ph
4g	Ph	Ph
4h	p-MeC$_6$H$_4$	Ph

Figure 1. Alkyne-inserted organometallics synthesized in the present work.



Ru(RL^1)(PPh$_3$)$_2$(CO)Cl

3

presence of primary amines (RNH$_2$).[14] The four-membered ring in **3** is known to undergo facile cleavage by ligands,[15,16] and this prompted us to explore the possible reactivity of **3** toward alkynes. A smooth and virtually quantitative reaction is indeed observed (eq 2) in a boiling dichloromethane-methanol mixture,

$$\underset{\mathbf{3}}{\mathrm{Ru(RL^1)(PPh_3)_2(CO)Cl}} + \mathrm{HC{\equiv}CX} \rightarrow \underset{\mathbf{4}}{\mathrm{Ru(RL^2,X)(PPh_3)_2(CO)Cl}} \quad (2)$$

$$\mathrm{X = H, Ph}$$

affording the insertion product Ru(RL^2,X)(PPh$_3$)$_2$(CO)Cl (**4**), which incorporates ring **2**. The alkynes used are acetylene and phenylacetylene. The eight species of type **4** (**4a**–**h**) are listed in Figure 1.

In previous studies only substituted acetylenes have been inserted into ruthenium–carbon bonds.[2,3d,9–13] Acetylene itself is successfully employed here (eq 2, X = H) for the first time.[17] The reaction of eq 2 also represents a rare[11] example of straightforward two-carbon metallacycle expansion uncomplicated by subsequent reactions.

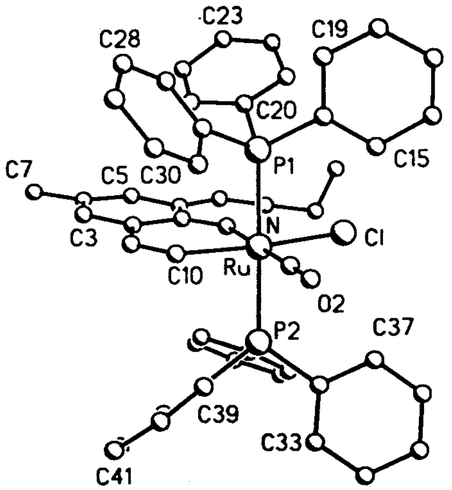


Figure 2. Perspective view and atom-labeling scheme for **4b**·CH$_2$Cl$_2$ (excluding CH$_2$Cl$_2$).

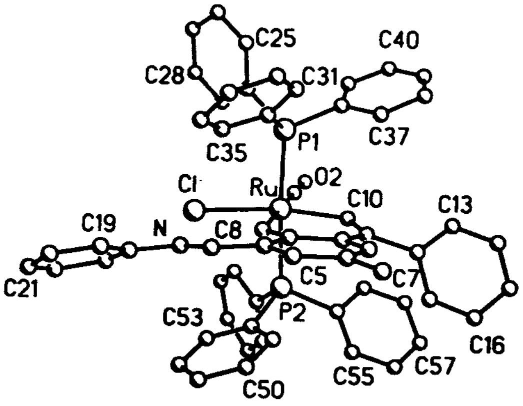


Figure 3. Perspective view and atom-labeling scheme for **4g**.

The type **4** species are diamagnetic and soluble in halocarbon solvents, affording green (R = aryl) or pink (R = alkyl) solutions. An allowed band in the 500–600 nm range (the range for the corresponding band in **3** is 480–540 nm[14]) is assigned to a $t_2 \rightarrow \pi^*$ MLCT transition which is blue shifted by ~60 nm on going from R = aryl to R = alkyl. In ^{1}H NMR the olefinic C=CH(Ru) protons resonate in the range δ 6.0–6.4 ($J_{HH} \approx 9$ Hz for X = H).

Structure. The X-ray structures of two representative compounds, viz. **4b**·CH$_2$Cl$_2$ and **4g**, have been determined, authenticating the insertion process. Molecular views are shown in Figures 2 and 3, and bond parameters are listed in Table 1. The RuC$_2$P$_2$ClO coordination sphere is distorted octahedral. The corresponding bond parameters of the two complexes are similar. The (σ-vinyl)phenolato chelate ring along with the benzene ring and the aldimine function (R and Me excluded), constitutes a good plane (mean deviation: **4b**·CH$_2$Cl$_2$, 0.03 Å; **4g**, 0.06 Å). The aryl rings at C9 and N in **4g** make dihedral angles of 122.5 and 24.8°, respectively, with the above plane.

The average Ru–C10 distance (2.034(10) Å) is slightly shorter than the usual Ru–C(σ-vinyl) lengths (~2.1 Å). The Ru–P, Ru–Cl, and Ru–C(carbonyl) lengths lie close

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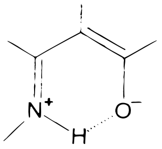
[17] Acetylene has however been inserted into the Ru–Si bond: Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1996**, *15*, 1793.

Table 1. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Ru(EtL^2,H)(PPh_3)_2(CO)Cl\cdot CH_2Cl_2$ ($4b\cdot CH_2Cl_2$) and $Ru(PhL^2,Ph)(PPh_3)_2(CO)Cl$ (4g)

	4b·CH_2Cl_2	**4g**
	Distances	
Ru−Cl	2.536(3)	2.540(3)
Ru−C10	2.040(9)	2.029(10)
Ru−P1	2.372(3)	2.372(3)
Ru−P2	2.372(3)	2.396(3)
Ru−O1	2.095(7)	2.100(7)
Ru−C11	1.809(10)	1.803(11)
O1−C1	1.287(12)	1.292(12)
O2−C11	1.149(12)	1.175(14)
N−C8	1.236(21)	1.323(15)
C9−C10	1.352(13)	1.346(13)
O1...N	2.556(12)	2.639(13)
	Angles	
Cl−Ru−P1	92.7(1)	95.2(1)
Cl−Ru−C10	163.4(3)	167.0(3)
P1−Ru−C11	88.8(3)	88.9(4)
Cl−Ru−O1	77.5(2)	81.5(2)
P1−Ru−C10	88.0(3)	90.5(3)
P1−Ru−P2	175.8(1)	176.0(1)
Cl−Ru−C11	101.2(3)	98.8(4)
C10−Ru−C11	95.3(4)	93.0(5)
P1−Ru−O1	91.0(2)	90.9(2)
O1−Ru−C10	85.9(3)	86.8(3)
O1−Ru−C11	178.7(4)	179.7(5)
Ru−C11−O2	179.5(7)	175.9(10)

to those in type **3** precursor complexes.[14] On the other hand, the average Ru−O1 length (2.098(7) Å) in **4b**·CH_2Cl_2 and **4g** is significantly shorter than that in the type **3** complex $Ru(MeC_6H_4L^1)(PPh_3)_2(CO)Cl$ (2.235(4) Å).[14b] Evidently the four-membered chelate ring of **3** is quite strained. Ring expansion via alkyne insertion increases the chelate bite angle from ~64° to ~87°, and the Ru−O(phenolato) bond becomes correspondingly shorter and stronger.

The Zwitterionic Iminium−Phenolato Function. The N···O1 lengths in **4b**·CH_2Cl_2 and **4g** (2.56(12) and 2.64(13) Å, respectively) are indicative of hydrogen bonding. The presence of the zwitterionic fragment **5**



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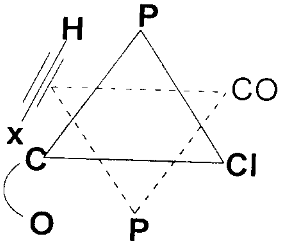
is consistent with IR and ^1H NMR data. The $N^+−H$ stretch occurs as a broad band of medium intensity in the region 3400−3440 cm^{-1}, suggesting the presence of relatively weak hydrogen bonding.[14,18] The C=N stretching frequency is relatively high (1620−1640 cm^{-1}), and this is consistent with the protonation of nitrogen.[14,18,19]

In compounds with R = aryl the iminium (δ 11.9−12.6; the signal disappears upon shaking with D_2O) and the azomethine (δ 6.9−7.4) ^1H signals are mutually split into well-resolved doublets, the coupling constant (~20 Hz) corresponding to trans disposition of the protons as in **5**. For R = alkyl species, the azomethine hydrogen is still a doublet but the $N^+−H$ signal is broadened, presumably due to additional coupling with alkyl protons (on α-carbon).

Regiospecificity: A Reaction Model. The reaction of eq 2 is not hindered by the presence of large excesses (10- to 50-fold) of either chloride ($LiCl/Et_4NCl$) or PPh_3 in the reaction solution. Therefore, the reaction does not appear to proceed via equilibrium dissociation of halide or phosphine ligands. Another crucial feature of the reaction is that phenylacetylene inserts regiospecifically, the ≡CPh and ≡CH carbons adding respectively to the carbon and metal ends of the Ru−C bond of **3**. In this manner the Ph group gets positioned anti to the metal site in **4** and is distanced from both PPh_3 and Cl. Interestingly, diphenylacetylene fails to insert into **3** under the conditions used for acetylene and phenylacetylene. These findings are indicative of a dominant steric control of the reaction path.

The Ru−O(phenolato) bond in **3** is known to be long (~2.24 Å),[9] being subject to facile reversible cleavage by ligands.[14−16,20] The initial π-anchoring of the alkyne to the metal is believed to be attended with Ru−O cleavage, as in **6**.[20] Subsequent 2 + 2 alkyne addition to the Ru−C bond is subject to steric crowding from the Cl and PPh_3 ligands (see **7**).[21,22]



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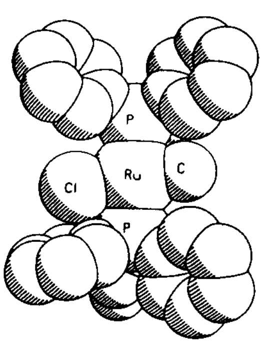

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The bulky ≡CPh end of phenylacetylene therefore adds to the carbon site. After insertion, the Ru−O bond is reestablished as in **4**. The inertness of diphenylacetylene to insertion is consistent with this model.

Oxidized Species. Organometallics incorporating trivalent ruthenium are scarce,[23] and this prompted us to explore the feasibility of generating ruthenium(III) congeners of **4**. In dichloromethane solution **4** was indeed found to display a quasireversible one-electron cyclic voltammetric response (eq 3) with $E_{1/2}$ in the range 0.3−0.4 V vs SCE (Table 2).

The $E_{1/2}$ values for X = Ph species are lower by 20−30 mV than those of the corresponding X = H species, as expected. Significantly, the $E_{1/2}$ values are much lower (by ~200 mV) than those of the corresponding

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(18) (a) Sandorfy, C.; Vocelle, D. *Mol. Phys., Chem., Biol.* **1989**, *4*, 195. (b) Chevalier, P.; Sandorfy, C. *Can. J. Chem.* **1960**, *38*, 2524. (c) Favrot, J.; Vocelle, D.; Sandorfy, C. *Photochem. Photobiol.* **1979**, *30*, 417.

(19) Bohme, H.; Haake, M. In *Advances in Organic Chemistry*; Bohme, H., Viehe, H. G., Eds.; Interscience: New York, 1976; Part 1, Vol. 9, p 1.

(20) To exclude steric repulsion between the entering ligand and the displaced phenolic oxygen, the cleavage process is associated with a 180° rotation of the RL^1 ligand around the Ru−C bond,[15,16] as implied in **6**.

(21) Diagram **7** was generated using coordinates of solved structures[9] of type **3** using the programs of SHELXTL-Plus.[22]

(22) Sheldrick, G. M. SHELXTL-Plus Structure Determination Software Programs; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990.

(23) Ghosh, P.; Pramanik, A.; Bag, N.; Lahiri, G. K.; Chakravorty, A. *J. Organomet. Chem.* **1993**, *454*, 237 and references therein.

Table 2. Cyclic Voltammetric Reduction Potentials[a] at 298 K

compd	$E_{1/2}$[M(III)−M(II)],[b] V (ΔE_p, mV)	compd	$E_{1/2}$[M(III)−M(II)],[b] V (ΔE_p, mV)
4a	0.35 (120)	**4e**	0.32 (100)
4b	0.34 (100)	**4f**	0.31 (170)
4c	0.37 (100)	**4g**	0.38 (160)
4d	0.39 (130)	**4h**	0.35(140)

[a] Conditions: solvent, dichloromethane; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, $\sim 10^{-3}$ M. [b] $E_{1/2} = 0.5(E_{pa} + E_{pc})$ at scan rate 50 mV s^{-1}, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$.

$$\mathrm{Ru^{III}(RL^2,X)(PPh_3)_2(CO)Cl^+} + e^- \rightleftharpoons \mathrm{Ru^{II}(RL^2,X)(PPh_3)_2(CO)Cl} \quad (3)$$

couples of complexes of type **3**.[14a] Coordination by the phenolato group, a hard donor, has been documented to stabilize trivalent ruthenium.[23,24] The lowering of $E_{1/2}$ values of **4** compared to those of **3** is associated with the strengthening of the Ru−O(phenolato) bond and formation of the Ru−C(vinyl) bond on going from **3** to **4**. The oxidized species in eq 3 were however found to be still too unstable for isolation via coulometry.

Concluding Remarks

The four-membered chelate ring of **3** smoothly expands by two carbon atoms upon insertion of acetylene/phenylacetylene, affording the new organometallic family **4**. The regiospecificity of phenylacetylene insertion and the inertness of diphenylacetylene are of steric origin. This work has provided the first examples of the insertion of unsubstituted acetylene into the Ru−C bond.

The hydrogen-bonded zwitterionic iminium-phenolato function is retained on going from **3** to **4**, even though during the insertion process the Ru−O bond is believed to be temporarily cleaved for initial anchoring of the alkyne. The Ru−O bond length and the $t_2 \rightarrow \pi^*$ MLCT exitation energy as well as the ruthenium(III)−ruthenium(II) reduction potential systematically decrease on going from **3** to **4**.

The RL^2 ligand in **4** is new, and we are trying to liberate it from **4** via demetalation with the objective of developing its organometallic chemistry with other transition metals.

Experimental Section

Materials. The starting materials $\mathrm{Ru(PPh_3)_3Cl_2}$[25] and $\mathrm{Ru(RL^1)(PPh_3)_2(CO)Cl}$[14] were prepared by reported methods. Phenylacetylene was obtained from Aldrich. The purification of dichloromethane and the preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were done as described before.[26] All other chemicals and solvents were of analytical grade and were used as received.

Physical Measurements. Electronic and IR spectra were recorded with Hitachi 330 and Perkin-Elmer 783 IR spectrophotometers. For ^{1}H NMR spectra a Bruker 300 MHz FT NMR spectrophotometer was used (tetramethylsilane is the internal standard). Magnetic properties were examined using a PAR 155 vibrating-sample magnetometer fitted with a Walker Scientific magnet. Microanalyses (C,H,N) were done by using a Perkin-Elmer 240C elemental analyzer. Electrochemical measurements were performed under a nitrogen atmosphere using a PAR 370-4 electrochemistry system. All potentials reported in this work are uncorrected for junction contribution.

Preparation of Complexes. The $\mathrm{Ru(RL^2,X)(PPh_3)_2(CO)Cl}$ (**4**) complexes were synthesized in nearly quantitative yields by reacting $\mathrm{Ru(RL^1)(PPh_3)_2(CO)Cl}$ with alkynes. Details are given for representative cases only.

[Ru(MeL^2,H)(PPh$_3$)$_2$(CO)Cl] (4a). The orange solution of $\mathrm{Ru(MeL^1)(PPh_3)_2(CO)Cl}$ (50 mg, 0.06 mmol) in a warm 1:4 mixture (50 mL) of dichloromethane and methanol was first purged with acetylene gas, and then the solution was heated to reflux for 5 h in an acetylene atmosphere with the help of a balloon filled with acetylene. The solution turned pink, and upon concentrating and cooling a pink crystalline solid separated, which was collected, washed thoroughly with methanol, and dried in vacuo. Yield: 51 mg (99%). Anal. Calcd for $\mathrm{RuC_{48}H_{42}NO_2P_2Cl}$: C, 66.78; H, 4.87; N, 1.62. Found: C, 66.82; H, 4.80; N, 1.59. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 6.17 (s, 1H arom), 6.52 (s,1H arom), 7.14−7.62 (m, 30H arom and 1H, CH=C(Ru)), 2.04 (s, 3H, $\mathrm{CH_3}$), 6.06 (d, 1H, C=CH(Ru), J_{HH} 9.0 Hz), 12.15 (s, 1H, =N$^+$H), 6.93 (d, 1H, −CH=N$^+$, J_{HH} 11.8), 2.62 (d, 3H, $\mathrm{NCH_3}$, J_{HH} 6.0). IR (KBr, cm^{-1}): ν(C=N) 1640; ν(C≡O) 1900; ν(N−H, hexachlorobutadiene) 3400. UV−vis ($\mathrm{CH_2Cl_2}$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 520 (2850), 370 (3880), 310 (9830). Complexes **4b**−**d** were prepared using the same procedure as above.

[Ru(EtL^2,H)(PPh$_3$)$_2$(CO)Cl] (4b). Using $\mathrm{Ru(EtL^1)(PPh_3)_2(CO)Cl}$ (50 mg, 0.058 mmol) a pink crystalline solid of **4b** was obtained. Yield: 50 mg (98%). Anal. Calcd for $\mathrm{RuC_{49}H_{44}NO_2P_2Cl}$: C, 67.08; H, 5.01; N, 1.59. Found: C, 66.98; H, 4.99; N, 1.63. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 6.22 (s, 1H arom), 6.55 (s, 1H arom), 7.17−7.61 (m, 30H arom and 1H, −CH=C(Ru)), 2.06 (s, 3H, $\mathrm{CH_3}$), 6.08 (d, 1H, C=CH(Ru), J_{HH} 8.9 Hz), 12.25 (s, 1H, =N$^+$H), 6.95 (d, 1H, CH=N$^+$, J_{HH} 11.2), 2.89 (q, 2H, NEt), 1.01 (t, 3H, NEt). IR (KBr, cm^{-1}): ν(C=N) 1640; ν(C≡O) 1895; ν(N−H, hexachlorobutadiene) 3400. UV−vis ($\mathrm{CH_2Cl_2}$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 520 (3240), 370 (3840), 310 (9490).

[Ru(MeC$_6$H$_4$L^2,H)(PPh$_3$)$_2$(CO)Cl] (4c). Using $\mathrm{Ru(MeC_6H_4L^1)(PPh_3)_2(CO)Cl}$ (50 mg, 0.054 mmol) a green crystalline solid of **4c** was obtained. Yield: 50 mg (98%). Anal. Calcd for $\mathrm{RuC_{54}H_{46}NO_2P_2Cl}$: C, 69.05; H, 4.90; N, 1.49. Found: C, 68.98; H, 4.96; N, 1.53. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 6.25 (s, 1H arom), 6.52 (s, 1H arom), 7.09−7.65 (m, 34H arom and 1H, CH=C(Ru)), 2.06 and 2.30 (2s, 6H, 2$\mathrm{CH_3}$), 6.13 (d, 1H, C=CH(Ru), J_{HH} 9.1 Hz), 12.87 (d, 1H, =N$^+$H, J_{HH} 21.0), 7.37 (d, 1H, −CH=N$^+$, J_{HH} 20.9). IR (KBr, cm^{-1}): ν(C=N) 1620; ν(C≡O) 1990; ν(N−H, hexachlorobutadiene) 3430. UV−vis ($\mathrm{CH_2Cl_2}$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 580 (3560), 428 (7010), 320 (10 460).

[Ru(ClC$_6$H$_4$L^2,H)(PPh$_3$)$_2$(CO)Cl] (4d). Using $\mathrm{Ru(ClC_6H_4L^1)(PPh_3)_2(CO)Cl}$ (50 mg, 0.053 mmol) a green crystalline solid of **4d** was obtained. Yield: 50.5 mg (99%). Anal. Calcd for $\mathrm{RuC_{53}H_{43}NO_2P_2Cl_2}$: C, 66.32; H, 4.48; N, 1.45. Found: C, 66.29; H, 4.50; N, 1.48. ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 6.25 (s, 1H arom), 6.58 (s, 1H arom), 7.13−7.76 (m, 34H arom and 1H, CH=C(Ru)), 2.06 (s, 3H, $\mathrm{CH_3}$), 6.12 (d, 1H, C=CH(Ru), J_{HH} 9.0 Hz), 12.82 (d, 1H, =N$^+$H, J_{HH} 20.9), 7.36 (d, 1H, −CH=N$^+$, J_{HH} 20.7). IR (KBr, cm^{-1}): ν(C=N) 1620; ν(C≡O) 1990; ν(N−H, hexachlorobutadiene) 3430. UV−vis ($\mathrm{CH_2Cl_2}$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 585 (3610), 430 (7380), 320 (12 950).

[Ru(MeL^2,Ph)(PPh$_3$)$_2$(CO)Cl] (4e). To a solution of $\mathrm{Ru(MeL^1)(PPh_3)_2(CO)Cl}$ (50 mg, 0.06 mmol) in a warm 1:4 mixture (50 mL) of dichloromethane and methanol was added phenylacetylene (30 mg, 0.30 mmol). The reaction mixture was heated to reflux for 1.0 h. Upon concentrating and cooling, a pink colored crystalline solid separated, which was collected,

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washed thoroughly with methanol, and dried in vacuo. Yield: 56 mg (99%). Anal. Calcd for $RuC_{54}H_{46}NO_2P_2Cl$: C, 69.04; H, 4.90; N, 1.49. Found: C, 68.90; H, 4.93; N, 1.51. ^1H NMR ($CDCl_3$, δ): 6.35 (s, 1H arom), 6.89 (s, 1H arom), 7.00−7.60 (m, 33H arom), 1.93 (s, 3H, CH_3), 6.27 (s, 1H, C=CH(Ru)), 11.87 (s, 1H, $=N^+H$), 6.95 (d, 1H, $-CH=N^+$, J_{HH} 11.7 Hz), 2.49 (d, 3H, NCH_3, J_{HH} 6.0), IR (KBr, cm^{-1}): ν(C=N) 1640; ν(C≡O) 1885; ν(N−H, hexachlorobutadiene) 3400. UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 520 (3940), 360 (5150), 310 (11 200). The following complexes (**4f**−**h**) were prepared using the same procedure as above.

$[Ru(EtL^2,Ph)(PPh_3)_2(CO)Cl]$ (4f). Using $Ru(EtL^1)(PPh_3)_2(CO)Cl$ (50 mg, 0.058 mmol), a pink crystalline solid of **4f** was obtained. Yield: 55 mg (99%). Anal. Calcd for $RuC_{55}H_{48}NO_2P_2Cl$: C, 69.29; H, 5.03; N, 1.46. Found: C, 69.31; H, 5.06; N, 1.45. ^1H NMR ($CDCl_3$, δ): 6.38 (s, 1H arom), 6.92 (s, 1H arom), 6.99−7.60 (m, 33H arom), 1.94 (s, 3H, CH_3), 6.32 (s, 1H, C=CH(Ru)), 12.01 (s, 1H, $=N^+H$), 6.98 (d, 1H, $-CH=N^+$, J_{HH} 11.0 Hz), 2.77 (q, 2H, NEt), 0.90 (t, 3H, NEt), 5.84 (d, 2H arom, J_{HH} 6.0 Hz). IR (KBr, cm^{-1}): ν(C=N) 1640; ν(C≡O) 1885; ν(N−H, hexachlorobutadiene) 3400. UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 520 (3760), 360 (5060), 310 (10 890).

$[Ru(PhL^2,Ph)(PPh_3)_2(CO)Cl]$ (4g). Using $Ru(PhL^1)(PPh_3)_2(CO)Cl$ (50 mg, 0.055 mmol) a green crystalline solid of **4g** was obtained. Yield: 54 mg (98%). Anal. Calcd for $Ru_{59}H_{48}NO_2P_2Cl$: C, 70.76; H, 4.79; N, 1.39. Found: C, 70.71; H, 4.82; N, 1.41. ^1H NMR ($CDCl_3$, δ): 6.42 (s, 1H arom), 7.00 (s, 1H arom), 7.02−7.70 (m, 38H arom), 1.94 (s, 3H, CH_3), 6.34 (s, 1H, C=CH(Ru)), 12.63 (d, 1H, $=N^+H$, J_{HH} 21.03 Hz), 7.37 (d, 1H, $-CH=N^+$, J_{HH} 15.0), 5.95 (d, 2H arom, J_{HH} 6.0). IR (KBr, cm^{-1}): ν(C=N) 1620; ν(C≡O) 1920; ν(N−H, hexachlorobutadiene) 3440. UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 585 (4330), 425 (8400), 320 (12 600).

$[Ru(MeC_6H_4L^2,Ph)(PPh_3)_2(CO)Cl]$ (4h). Using $Ru(MeC_6H_4L^1)(PPh_3)_2(CO)Cl$ (50 mg, 0.054 mmol) a green crystalline solid of **4h** was obtained. Yield: 54 mg (98%). Anal. Calcd for $RuC_{60}H_{50}NO_2P_2Cl$: C, 70.97; H, 4.92; N, 1.37. Found: C, 71.10; H, 4.96; N, 1.41. ^1H NMR ($CDCl_3$, δ): 6.41 (s, 1H arom), 7.01 (s, 1H arom), 7.02−7.68 (m, 37H arom), 1.93 and 2.30 (2s, 6H, $2CH_3$), 6.33 (s, 1H, C=CH(Ru)), 12.64 (d, 1H, $=N^+H$, J_{HH} 20.1 Hz), 7.35 (d, 1H, $-CH=N^+$, J_{HH} 13.1), 5.96 (d, 2H arom, J_{HH} 6.0). IR (KBr, cm^{-1}): ν(C=N) 1620; ν(C≡O) 1900; ν(N−H, hexachlorobutadiene) 3440. UV−vis (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 585 (4040), 425 (8170), 320 (12 960).

Attempted Reaction between $[Ru(MeC_6H_4L^1)(PPh_3)_2(CO)Cl]$ and Diphenylacetylene. To a solution of $Ru(MeC_6H_4L^1)(PPh_3)_2(CO)Cl$ (50 mg, 0.06 mmol) in a warm 1:4 mixture of dichloromethane and methanol was added diphenylacetylene (107 mg, 0.60 mmol). The reaction mixture was heated to reflux up to 3.0 h. No green coloration appeared, and the reaction mixture consisted of starting materials only.

X-ray Structure Determination. The single crystals of $Ru(EtL^2,H)(PPh_3)_2(CO)Cl.CH_2Cl_2$ (**4b**·CH_2Cl_2; 0.20 × 0.40 × 0.40 mm^3) and $Ru(PhL^2, Ph)(PPh_3)_2(CO)Cl$ (**4g**; 0.25 × 0.20 × 0.30 mm^3) were grown (at 298 K) by slow diffusion of hexane into dichloromethane solution followed by evaporation. Cell parameters were determined by a least-squares fit of 30 machine-centered reflections ($2\theta = 15-30°$). Data were collected by the ω-scan technique in the range $3° \leq 2\theta \leq 45°$ on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Two check reflections measured after every 198 reflections showed no significant intensity reduction in any cases. All data were corrected for Lorentz-polarization effects, and an empirical absorption correction[27] was done on the basis of an azimuthal scan of six reflections for each crystal.

Table 3. Crystal, Data Collection, and Refinement Parameters for 4b·CH_2Cl_2 and 4g

	4b·CH_2Cl_2	**4g**
mol formula	$C_{50}H_{46}Cl_3NO_2P_2Ru$	$C_{59}H_{48}ClNO_2P_2Ru$
mol wt	962.2	1001.4
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	12.129(4)	14.845(6)
b, Å	28.336(9)	15.010(4)
c, Å	13.349(5)	22.003(7)
β, deg	90.29(3)	93.57(3)
V, Å^3	4587(3)	4922(3)
Z	4	4
λ, Å	0.710 73	0.710 73
μ, cm^{-1}	6.28	4.84
F(000)	1976	2064
D_{calcd}, g cm^{-3}	1.396	1.356
temp, °C	22	22
R,[a] %	6.36	6.02
R,[b] %	7.30	6.94
GOF[c]	1.27	1.30

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(||F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2|F_o| + g|F_o|^2$; $g = 0.0005$ for **4b**·CH_2Cl_2 and 0.0003 for **4g**. [c] The goodness of fit is defined as $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

In each case the metal atom was located from a Patterson map and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structures were refined by full-matrix least-squares procedures. The NEt group in **4b**·CH_2Cl_2 is disordered. All non-hydrogen atoms except for the NEt group in **4b**·CH_2Cl_2 were refined anisotropically, and hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2. The highest residuals were 1.43 e Å^{-3} (**4b**·CH_2Cl_2) and 1.07 e Å^{-3} (**4g**). All calculations were done on a Micro Vax II computer using the SHELXTL-PLUS program package.[22] Significant crystal data are listed in Table 3.

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Supporting Information Available: For $Ru(EtL^2,H)(PPh_3)_2(CO)Cl\cdot CH_2Cl_2$ (**4b**·CH_2Cl_2) and $Ru(PhL^2,Ph)(PPh_3)_2(CO)Cl$ (**4g**) tables of all bond distances (Tables S1 and S6) and angles (Tables S2 and S7), anisotropic thermal parameters (Tables S3 and S8), hydrogen atom positional parameters (Tables S4 and S9), and non-hydrogen atomic coordinates and U values (Tables S5 and S10) (13 pages). Ordering information is given on any current masthead page.

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